A METALLOGRAPHIC STUDY
ON
TUNGSTEN STEELS

BY
AXEL HULTGREN
METALLURGICAL ENGINEER

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PREFACE

THE metallographic investigations, which form the main part of the present treatise, were originally undertaken at the Institute of Technology of Charlottenburg, Germany, in 1913 to 1914. They were further developed and completed during 1914 to 1918 at K. Tekn. Högskolans Materialprofningsanstalt (Royal Institute for Testing Materials) Stockholm and in the Laboratory of A. B. Svenska Kullagerfabriken (SKF Ball Bearing Co.), Gothenburg, Sweden.

The constitution and transformations of tungsten steels which are the subject of this work have been studied by several investigators. The views arrived at by them are, however, partly rather general and partly conflicting among themselves. Consequently, they do not give a clear conception of the laws and phenomena involved. By presenting certain new facts and new problems and critically examining previous results and opinions, it is believed that the present study, however incomplete, constitutes a step towards a clearer understanding of tungsten steels. It may also be of value for the study of other alloy steels and carbon steels.

The paper was written in Swedish in 1918. In its present form it includes a translation of the Swedish paper as well as an appendix, containing a critical review of investigations on tungsten steels, published in 1917 and 1918, but until last year unknown to the author.

The author wishes to express his gratitude to Professor H. Hanemann, Charlottenburg, for his initiative in starting this work and for his valuable assistance and interested cooperation in the earlier part of its development. The author is also indebted to K. Tekn. Högskolans Materialprofningsanstalt, Stockholm, and A. B. Svenska Kullagerfabriken, Gothenburg, for the permission

given to continue and conclude his investigations; to various steel works, which furnished steel samples and to the associates of the Laboratory of A. B. Svenska Kullagerfabriken, which assisted him in carrying out experiments.

AXEL HULTGREN.

PHILADELPHIA, SKF RESEARCH LABORATORY,
February, 1920
Permanent address:
GOTHENBURG, SWEDEN.

INTRODUCTION TO THE AUTHOR'S STUDY ON TUNGSTEN STEELS

THE author's study does not include high-speed steel or other quaternary steels containing tungsten, but only ternary tungsten steels. It was not made according to a predetermined plan, involving a great number of tungsten steels of different tungsten and carbon contents. To begin with, only a few available tungsten steels were subjected to microscopic investigation after different heat treatments, mainly with the object in view of ascertaining the nature of the "lowering" or "splitting" of Ar_1 under cooling from high temperature. For elucidating these phenomena and other problems encountered during this work a great number of cooling experiments were found to be required. Also different free carbides were observed in these steels, for the study of which the investigation was extended to comprise other tungsten steels and iron-tungsten-carbon alloys. The data obtained were finally brought together to form the basis of a tentative iron-tungsten carbon equilibrium diagram.

Accordingly the subject is divided in two sections:

(1) The transformations of tungsten steels during different heat treatments and the structures thereby formed.

(2) Carbides in tungsten steels.

Each of these two sections is introduced by a review of the previous knowledge of the subject in question, as represented by the results and views of previous investigators. They are given as quotations or extracts from published papers, and are presented without any comments by the present author. The views represented are in certain respects rather contradictory, but will be better understood, after the author's results and conclusions are developed. These are presented in the order they were actually obtained, as a natural consequence of the fact, that most of the author's experiments were undertaken to illustrate

and clarify doubtful questions met with in the course of investigation. A review of the results obtained and conclusions arrived at is given at the end of each section. This review is followed by a critical examination of the results of previous investigators, seen in the light of the author's results.

Finally, a summary is given of the whole study.

Unfortunately, this work was concluded before the important investigations on tungsten steels by Honda and Murakami became known to the author. A critical examination of their results has, however, been added as an appendix on p. 79.

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A METALLOGRAPHIC STUDY ON TUNGSTEN STEELS

I. THE TRANSFORMATIONS OF TUNGSTEN STEELS DURING DIFFERENT HEAT TREATMENTS AND THE STRUCTURES THEREBY FORMED

A. PREVIOUS INVESTIGATIONS

The results and views of previous investigators are given in the following:

F. Osmond, 1892.[1] A tungsten steel, containing 6.22 per cent W and 0.42 per cent C, showed on cooling from 920° C. two recalescence points, the upper at about 680° C., and the lower about 30–40° C. lower. On cooling from higher temperatures than 920° C. the upper recalescence point retained about the same position, while the lower one dropped by degrees to about 500° C. (corresponding to a maximum heating temperature of 1210° C.).

F. Osmond, 1904.[2] "The effect of the presence of allied metals, such as chromium and tungsten, is to obstruct during cooling the segregation of cementite sufficiently for one to be able as a first approximation to neglect the variations of the rate of cooling within certain limits and to a certain degree. This is an experimental fact. It results in the transformation point being lowered in cooling, even slow cooling in proportion as the quantity is raised above the eutectoid composition. Of the two factors, carbon content and rate of cooling, utilized in

[1] Reported in R. A. Hadfield, "Alloys of Iron and Tungsten," The Journal of the Iron and Steel Institute, 1903, II, p. 14.

[2] "Contribution a la Théorie des aciers rapides," Revue de Métallurgie, 1904, p. 348.

pure carbon steels to obtain the whole gamut of structural constituents, the second can be quite eliminated. The first by itself permits the same result to be obtained."

He expressed further, with regard to these steels that, just as the segregation of carbon during cooling is rendered difficult, its solution on heating is equally affected. There is consequently a temperature range above $Ac_{3.2.1}$, in which the solution of the carbon on heating is incomplete, so that the carbon content is unevenly distributed in different parts of the mass. If the steel is cooled down from such a temperature, each fraction behaves as if it were alone and its recalescence occurs at a temperature which is a function of its carbon content. The frequent doubling of the recalescence point is thus explained.

O. Böhler, 1904.[1] A tungsten steel with 7.78 per cent W and 0.85 per cent C showed on cooling from:

850° C.: a recalescence point at 700° C.[2]

950° C.: a recalescence point at 690° C., weaker than the previous one.

1050° C.: an upper recalescence point, still weaker, at 670° C. and a weak, lower one at 595° C.

1100° C.: an almost imperceptible upper point and a strong lower one, which begins at 590° C., and is intensified at 550° C.

1150° C.: a lower and still stronger point, which begins at 580° C. and is intensified at 540° C.

His experiments were carried out in a Heraeus furnace and the specimens were allowed to cool in the furnace. Experiments with tungsten steels of other compositions gave similar results. He draws the following conclusions:

(1) Through raising the initial temperatures (800–1150° C.) from which cooling begins, the upper recalescence point is steadily lowered and weakened and the lower one, lowered and strengthened; so that on cooling from a low initial temperature only the upper recalescence point appears, while from a high initial temperature only the lower one is found.

(2) The higher the tungsten content the lower the tem-

[1] "Wolfram- und Rapidstahl," Vienna, 1904.

[2] The recalescence temperatures mentioned refer to the beginning of the recalescence; Böhler, on the other hand, considers its end.

perature at which the low recalescence point appears, and also the lower the initial temperature required for its appearance.

(3) After the steel has been heated to a high temperature, the condition obtained cannot be altered by, for example, cooling down from the high temperature to the low initial temperature (about 800° C.) and holding there for half an hour, but even in this case there appears only one recalescence point, i.e., the lower one.

(4) The maintenance of the initial temperature for a considerable time before the cooling has to a certain extent the same effect as if it were raised.

(5) The lowering of the recalescence point is probably not due to a decrease in the rate of transformation, because the lowering is equally marked when the cooling is carried on more slowly.

(6) Both recalescence points, the upper as well as the lower, correspond to a formation of pearlite.

L. Guillet, 1905.[1] Steels with different tungsten and carbon contents were investigated.

Air Hardening Experiments from Different Temperatures (800–1200° C.)

When W <2 per cent, hardening does not occur.

When W >2 per cent, the steel becomes hardened at the surface as soon as the hardening temperature reaches 900° C. Martensite and patches of troostite are formed thereby; the latter decreasing in quantity as the hardening temperature is raised.

Annealing Experiments, Four Hours at 900° C., Slow Cooling

In the case of lower tungsten contents the steels become pearlitic when annealed in the same way as carbon steels.

H. C. H. Carpenter, 1905.[2] The critical points and ranges of two tungsten steels were determined (in connection with an investigation of high-speed steel) with the following results:

[1] "Aciers au tungstène," Revue de Métallurgie, 1904, p. 263.

[2] "The types of structure and the critical ranges on heating and cooling of high-speed tool steels under varying thermal treatment," The Journal of the Iron and Steel Institute, 1905, I, p. 433.

W Per Cent.	C Per Cent	Initial Temperature.	Critical Points and Ranges.		
0.94	0.25	1000° C.	800°–782° C.	760°–746° C.	690° C.
		1250° C.	800°–606° C.	782°–664° C.	
		1000° C.	806°–782° C.	760°–746° C.	686° C.
10.56	0.63	900° C.	.....	768°–712° C.	712°–700° C.
		1207° C.	.....	783°–735° C.	550°–440° C.

L. Guillet, 1906.[1] "W lowers the transformation points of the carbon."

Th. Swinden, 1907.[2] Cooling experiments from different initial temperatures were made with steels of W = about 3 per cent and different carbon contents (0.14–1.24 per cent).

"Below a certain initial temperature all the steels examined show critical points as for carbon steels.

"In steels below 0.35 per cent carbon, heating beyond this initial temperature lowers Ar_1 to a definite low point; Ar_2, is practically unaffected; Ar_3 is gradually suppressed in its normal position, but appears again below Ar_2 forming the upper maximum of the low point.

"With carbon contents 0.35 to 0.9 per cent Ar_1 is first lowered, and then increased heating displaces $Ar_{3.2}$ towards Ar_1. Beyond 0.9 per cent carbon, the $Ar_{3.2.1}$, point is lowered as a whole by heating beyond the lowering temperature,[3] and produces a single low point.

"As the carbon increases, higher initial temperature is needed for the lowering to be effected.

"The low point is practically constant at 570° C. for 3 per cent tungsten steels.

"Rate of cooling does not affect the position of the low point after lowering has once taken place.

"The range of recalescence is not merely widened, but the critical point is at a distinctly lower temperature.

"At Ac_1, on heating, a change of similar nature to the

[1] "Etude industrielle des alliages métalliques," Paris, 1906.

[2] "Carbon-tungsten steels," The Journal of the Iron and Steel Institute, 1907, I, p. 291.

[3] This term is used by Swinden to indicate the temperature which has to be reached on heating in order that the low point may appear on cooling.

carbon change occurs; and at the lowering temperature a further change in constitution takes place, the reverse of which is at the low point.

"No recalescence has been found at the lowering temperature.

"Microscopic examination confirms the cooling curves, showing the eutectic composition practically unaltered. The structures resemble carbon steels, but are finer in pattern."

C. A. Edwards, 1908.[1] The investigation concerns high-speed steel principally.

"The low transformation point is not Ar_1 lowered by tungsten, but a carbide of tungsten is slowly formed at about 1200° C., which has a critical temperature quite independent of Ar_1."

Th. Swinden, 1909.[2] This investigation forms a continuation of the 1907 investigation on steels with about 3 per cent W. He offers the following tentative hypothesis regarding the constitution of tungsten steels:

In the steel Fe_3W exists, separated in the mass. On heating to the lowering temperature this goes into solution and in this new solution the Fe_3C is dissolved. The Fe_3W does not separate again, until the low point is reached and then the Fe_3C is immeditely separated also.

P. Dejean, 1917.[3] The appearance of two transformation points on cooling can be seen in all alloy steels, when the proper initial temperature is used. The higher of these points corresponds with a formation of troostite and the lower with a formation of martensite, both being formed from austenite.

B. THE AUTHOR'S INVESTIGATIONS

Composition

The compositions of the steels, upon which the experiments were made are given in the following Table I:

[1] "Function of Chromium and Tungsten in High-speed Tool Steel," The Journal of the Iron and Steel Institute, 1908, II, p. 104.

[2] "The Constitution of Carbon-tungsten Steels," The Journal of the Iron and Steel Institute, 1909, II, p. 223.

[3] "Les points critiques de refroidissement des aciers auto-trempants et la formation de la troostite et la martensite," Revue de Métallurgie, 1917, p. 641.

TABLE I

Mark.	C Per Cent.	W Per Cent.	Si Per Cent.	Mn Per Cent.
B1	0.75	1 6	0.10	0.31
B2	0.95	0.95	0.14	0.33
B3	0.94	2.9	0.14	0.42
B5	1.29	4.8	0.20	0.33
6	0.61	6.4	0.06	

The Si and Mn contents are low or moderate and are supposed not to influence the results to any material degree.

The steels marked B were in the form of drawn wire measuring 5 mm. in diameter: steel No. 6 was forged to $\frac{1}{2}$ in. square. All were annealed.

Experimental Methods

In studying the nature of the singular transformations which are characteristic of tungsten steels on cooling from high temperatures, it was expected by the author that fixing of the actual structure at different stages of the cooling process by quenching the specimen in water would give valuable information. This method, therefore, has been extensively used and with good results. Any possible errors which may arise are due to the transformations which may take place during the quenching itself. As a matter of fact the formation of martensite out of austenite is the only one needed to be taken into consideration, since troostite could not form during quenching on account of the tungsten content present and the small dimensions of the test specimens. When two or more transformations occur at different temperatures during the cooling process, it is evidently impossible to determine what has taken place at each of these transformations by merely examining the structure after cooling down to normal temperature.

The heating and cooling experiments were carried out in a Heraeus furnace, which was allowed to cool by itself or was regulated in such a manner as to obtain the desired cooling rate. The temperature was measured by means of a platinum platinum-rhodium thermocouple which had been calibrated with a standard couple.

A glazed china tube—15 mm. in diameter—was inserted from one end into the middle of the furnace. The test specimens, the lengths of which were about 3 cm. in the case of steels B1, B2, B3 and B5—and 1 cm. steel No. 6—respectively, were placed in the inner end of this tube, the hot junction of the thermo-couple being placed in contact with them. A steady stream of nitrogen was allowed to pass through the tube in order to prevent the oxidation and decarbonization of the test specimens. In order to purify the nitrogen from traces of oxygen the inner

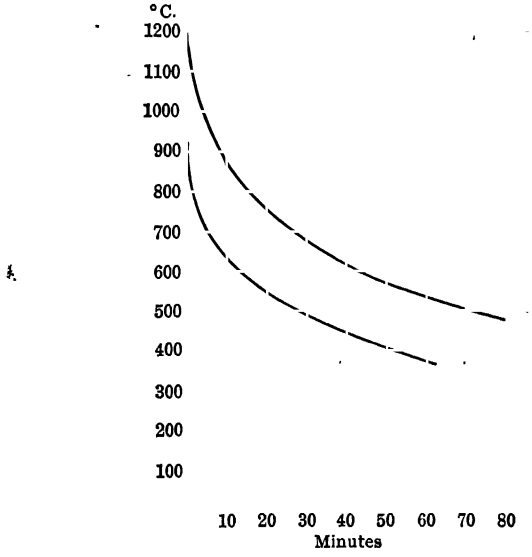


FIG. 1.

part of the tube was filled with drillings of cast iron. This arrangement proved very efficient in preventing decarboniza-tion. In some of the experiments the stream of nitrogen was omitted in order that the structure of the decarbonized outer layer of the specimen might be studied and compared with that of the central portion. The heating tube of the furnace was closed at each end by means of a plug.

The test specimens were provided with iron wires, which were fastened to them and allowed to protrude from one end of the furnace. By this means any specimen could at a given moment

be quickly withdrawn from the furnace. The specimen was then quenched or cooled in the air either to room temperature or a temperature judged by the eye to match the temperature of another Heraeus furnace, in which the specimen was then inserted, and allowed to remain there for a certain period, whereupon it was quenched.

In the cooling experiments, except when stated otherwise, the initial temperature was always maintained for five minutes before cooling began. The rate of cooling from 1200 and 910° C. respectively, is shown by Fig. 1.

Where a temperature was kept constant for a certain length of time, the accuracy of same was always within ±4°C. Quenching was always done in water.

One per cent solution of nitric acid in alcohol was generally used as an etching reagent for the microscopic examination. In order to distinguish different carbides present either etching in boiling sodium picrate solution or heat tinting was used.

THE EXPERIMENTS AND THEIR RESULTS

Steel B3; C=0.94 Per Cent, W=2.9 Per Cent

The larger part of the experiments made were carried out on this steel.

To begin with the following data may be given regarding its structure:

In the *annealed* steel a very uniform structure was observed, consisting of small globular grains of cementite in ferrite: i.e., granular pearlite.

In the *hardened*, martensitic specimens a number of thinly distributed small grains of a gray-white color was revealed on close examination at high magnification. The appearance of this constituent was rather characteristic: it had apparently a great hardness, since it was raised above the surrounding martensite and showed a rounded surface. It was not affected by boiling sodium picrate and showed the highest resistance to heat tinting of all constituents present.

By a special investigation, which will be described later, it was ascertained, that this constituent was *mono-tungsten carbide, WC.*

WC was present in all the specimens of this steel, in the annealed as well as in the hardened. It is to be expected that the solubility of this carbide in austenite increases at higher temperatures. This could, however, not be proved by microscopic examination. The quantity present in specimens hardened from different temperatures above Ac_1 was always small and apparently the same.

Fig. 2 shows a heating and cooling curve previously obtained on a sample of this steel at the Metallographical Laboratory in

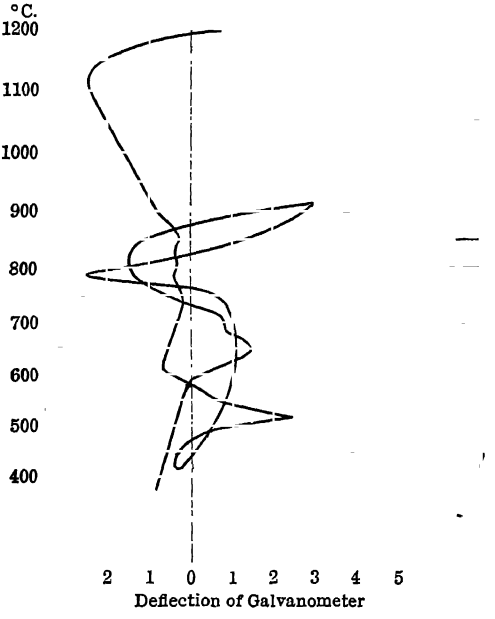


FIG. 2.

Charlottenburg by the use of a Saladin apparatus. The experiment was carried out in a Heraeus furnace.

The curve begins at 1200° C., from which temperature the specimen (a number of wire pieces) was allowed to cool down in the furnace to 420° C. The temperature was then gradually raised to 910° C., and a second cooling curve taken from this temperature.

In the three branches of the curve the following critical points and ranges are to be seen, the temperatures given referring to the beginning of the transformations.

(*a*) Cooling curve from 1200° C.,
A weak critical point at 875° C.,
A weak critical point at 770° C.,
A strong critical point at 610° C., continuing to:
A still stronger critical point at 550° C., continuing to 515° C., or four critical points in all.

(*b*) Heating curve.
A strong critical point, Ac_1, at 780° C.

(*c*) Cooling curve from 910° C.
A strong critical point at 800° C., continuing to 700° C.
A strong critical point at 675° C., continuing to 650° C.

As already mentioned, numerous cooling experiments, interrupted by quenching, were carried out in order to fix the structures at different temperatures during cooling. The first series of experiments on this steel were made so as to conform to the curves given, thereby using the same initial temperatures 910 and 1200° C. The results obtained from microscopic examination of the quenched specimens were compared with the indications given by the curves. Later cooling from intermediate temperatures 1000 and 1100° C., was studied. All conclusions to be made regarding transformations rest upon the structural investigation. The results of these experiments were as follows:

Cooling from 910° C.

910° Q:[1] Martensite (see photo No. 1).

910° furnace 732° Q:[1] Martensite with small amounts of ferrite separated at the surface of the specimen, indicating decarbonization. As these ferrite separations were concentrated at equal distances on four points of the circumference, it is evident that the decarbonization originates from a previous heating of the square billet before rolling, the corners of the square section being more exposed to heat and oxidation than the sides.

[1] The abbreviated terms introduced here, indicating the heat treatment of the specimens, should be readily understood, for instance: "910° Q." means that the specimen was kept at 910° C., for five minutes and then quenched; "910° furnace 732° Q." means that the specimen was kept at 910° C. for five minutes and then allowed to cool down to 732° C. in the furnace, whereupon it was quickly removed and quenched.

910° furnace 700° Q: Similar to the previous one; the ferrite separations have, however, increased and in connection with them small grains of pearlite of indistinct structure appear.

910° furnace 675° Q: The formation of ferrite and pearlite has proceeded further inwards, still confined, however, to the surface portion of the specimen. The main body continues to consist of martensite.

910° furnace 644° Q: The ferrite occupies the same area as in the previous specimen, the remainder being pearlite, the structure of which, as is seen from photo No. 2, is ill-defined and not resolved by the microscope.

The results of the microscopic examination agree in all respects with the cooling curve from 910° C. The lower transformation, seen on the curve to start at 675° C. is Ar_1, the austenite here completely transforming into pearlite. The upper critical point, which begins at 800° C., represents what may be termed an unnatural transformation, viz., the $Ar_{3.2}$ or Ar_3 of the decarbonized surface layer.

It should be noticed that pearlite was formed already at 700° C. when in connection with ferrite, whereas, the main part of the specimen did not have its pearlite transformation until 675° C. was passed. The conclusion is that ferrite grains present act as nuclei for pearlite formation, thus causing this to begin in these portions at a higher temperature than would otherwise have been the case. It is also very possible, that on slower cooling Ar_1 would have occurred at a higher temperature than 675° C., even in the central portion of the specimen.

To clear up this matter and definitely to ascertain the *position of Ar_1 on very slow cooling from 910° C.* the following experiments were made:

910° furnace 725° 2h. Q:[1] The main body consists of *martensite.* In this grains of cementite are found of branch-like form (forming an incomplete network, indicating the size of the austenite grains, from which the cementite was separated). Small grains of ferrite appear beside some of the cementite grains, indicating that the pearlite formation has just begun.

[1] By regulating the heating current the specimen was kept at 725° C. for two hours, after which it was quenched.

The structure is seen in photo No. 3, where the cementite is colored dark by etching in sodium picrate.

The experiment proves that this steel is *hyper-eutectoid*. The cementite did not, however, appear on normal cooling (in the furnace) from 910° C., which was evidently due to the fact that the cooling rate was too fast (at 750° C. : 35° per minute).

910° furnace 715° 2h. Q: The pearlite has increased and shows a fine granular structure. Further appear in the martensite, separate small grains of unknown nature, too small to permit a closer examination. They may be called *Y-grains*. This constituent was also found in steel B5 after similar treatment; on account of the small size of the grains, however, it was impossible to determine their qualities with any degree of certainty.[1]

The structure of this specimen is seen from photo No. 4. In the middle of the larger mass of pearlite lies a large branched cementite grain.

910° furnace 710° 1h. furnace 700° 1h. Q: Entirely pearlite (granular or finely agglomerated) with large grains of hyper-eutectoid cementite.

From this series of experiments it can be concluded that if on cooling from 910° C. sufficient time is allowed for pearlite to form; this will take place at a temperature somewhat above 725° C. In other words, the position of Ar_1, on cooling from 910° C. varies with the rate of cooling to such a degree that the normal cooling in the furnace will cause an undercooling of this transformation of more than 50° C.

Furthermore, when compared with carbon steel, it is found that the tungsten content raises Ar_1.

It may accordingly be stated, that *tungsten raises the pearlite transformation point and retards the transformation, so that with ordinary cooling rates it takes place at a lower temperature, even when the initial temperature has been as low as 910° C.*

[1] Judging from magnetic cooling curves, presented by Honda and Murakami (see Appendix), there are reasons to believe that these minute grains consist of WC.

Cooling from 1200° C.

1200° Q:
1200° furnace 900° Q:
1200° furnace 800° Q:
} Coarse-needled martensite with small areas of austenite. Small grains of WC as usual.

1200° furnace 750° Q: Principally the same structure as just described. In the decarbonized portion of the surface *ferrite* grains appear to a depth varying between 0 and about 0.2 mm.

1200° furnace 720° Q: The main mass is still martensitic. The ferrite grains at the surface have now penetrated to a maximum depth of about 0.3 mm. In the main central portion of the cross-section appear long narrow seams of *cementite*, separated in the boundaries of the pre-existing austenite grains indicating their size. This structure may be seen in photo No. 5.

1200° furnace 650° Q: Martensite, cementite, and ferrite (at the surface) appear as in the previous specimen. In addition small *troostite* areas have been formed, generally adjoining the cementite seams. This structure may be seen from photo No. 6.

1200° furnace 584° Q: The formation of troostite has now proceeded so far that it occupies about one-third of the entire mass. At a high magnification a few minute separations can be seen forming needles or seams adjoining the troostite grains (see the following specimen). The structure is shown on photo No. 7.

1200° furnace 540° Q: The structure of this specimen, which is exceedingly interesting, is shown in photos Nos. 8, 9 and 10 (magnified 150,500 and 1200 diameters respectively). It is clearly seen that large quantities of a white constituent have separated from the still untransformed portions of austenite; this separation evidently took place after the troostite formation which seems not to have proceeded after a temperature of about 584° C. was reached. It may be described partly as seams adjoining and surrounding the previously formed troostite grains, partly as needles, located inside the austenite grains and following their cleavage planes, thus resulting in a distinct Widmann-

stätten structure. This white constituent, present in all tungsten steels (subjected to a similar treatment) examined by the author,[1] is *ferrite*, as is proved by the following facts:

It is quickly etched by 1 per cent nitric acid as is common ferrite.

It is not colored by boiling sodium picrate.

It is soft and may be scratched with a needle.

When found together with ordinary ferrite, separated on cooling through the critical range about 800 to 700° C., of a hypo-eutectoid tungsten steel, it forms continuous grains, with the latter.

Of the two varieties of ferrite, the one formed at the lower temperature may be called *secondary ferrite* and the other *primary ferrite*. The former is easily distinguished from the latter by its Widmannstätten arrangement.

The structure of the decarbonized steel near the surface of the same specimen is illustrated in photo No. 11. On comparison with photo No. 9 it will appear that the surface portion shows a smaller amount of troostite, indicating that a higher carbon content favors the troostite formation.

1200° furnace 515° Q: The structure is shown on photo No. 12. The separation of ferrite has now advanced so far that the main mass has a shattered appearance. The solid solution has a darker color than before, either due to the etching (caused by the finely divided, alternating arrangement with ferrite) or to a decomposition of the austenite during the cooling from 540° to 515° C.

1200° furnace 500° Q: Similar to the previous one (see photo No. 13). It can, however, now be stated with certainty that no martensite is present. The remains of the solid solution, i. e., the small portions lying between the needles of ferrite, are exceedingly narrow and dark in color.

It is obvious that the ferrite separation is accompanied by an increase in the carbon content of the remaining solid solution. This, as well as the lower temperature, may have favored its decomposition.

1200° furnace normal temperature: Quite similar to the

[1] Provided the tungsten content exceeds 1 per cent.

previous one. Consequently, after 500° C. is passed, no further transformation takes place.

By the microscopical examinations made the following has been found as to the transformations occurring in steel B_3 during cooling in the furnace from 1200° C.

(1) Between 800 and 750° C. separation of *primary ferrite* begins in the decarbonized surface layer of the steel.

(2) Between 750 and 720° C. separation of excessive *cementite* begins in the main body of the steel, in the boundaries of the austenite grains.

(3) At about 650° C. the austenite begins to decompose into *troostite* at different points in the mass. This transformation proceeds gradually, until the troostite occupies about one-third of the entire mass; this is the condition at 584° C. Then it ceases and

(4) A vigorous separation of *secondary ferrite* sets in at about 584° C. How far down this separation continues cannot be exactly determined by the structure of the quenched specimens, probably, however, to about 515° C.

(5) What happens next is very uncertain, as the only indication found in the structure is a uniform darkening of the remaining solid solution. Probably this corresponds to a decomposition of the austenite.

In comparing these results with the critical points of the cooling curve no close agreement is found. The two vigorous heat evolutions starting at 610 and 550° C. probably correspond to the troostite and secondary ferrite formations which, in the cooling experiments began at about 650 and 580° respectively. No attempt will be made to explain the discrepancy between the weak critical points at 875 and 770° C. on the curve and the primary ferrite and cementite separations which were found in the cooling experiments to occur, the former between 800 and 750° C. and the latter between 750 and 720° C.

The differences in the transformations occurring during continuous cooling from 910° C. and from 1200° C. are briefly:

On cooling from 910° C. a complete decomposition of the austenite into pearlite takes place in the temperature range between 675 and 650° C. No excessive cementite is separated.

On cooling from 1200° C.

(1) Cementite is separated somewhere between 750 and 720° C.[1]

(2) The decomposition of austenite into troostite starts at about 650° C. and continues to about 580° C., when it ceases without being entirely completed.

(3) From the remaining austenite (about two-thirds of the mass) secondary ferrite is separated in the temperature range from 580 to 515° C.

(4) The austenite still remaining probably decomposes.

It is evident, therefore, that heating of the steel from 910 to 1200° causes a change in the austenite such that the rate of pearlite formation during cooling is decreased. The result is that this transformation starts at a lower temperature and is never completed. It may also be true that the Ar_1 point is actually lowered.

The latter question was settled by the following *experiments with slow cooling from 1200° C.* which also give information as to the *cementite separation on slow cooling.*

1200° furnace 600° 1h. Q: Photo No. 14 shows that only part of the mass remains as solid solution, the balance being transformed to troostite.

1200° furnace 600° 3h. Q: The structure consists almost entirely of troostite, only very small martensite areas being seen (see photo No. 15).

It is thus evident that the austenite, during cooling from 1200°, changes entirely into troostite, if sufficient time is allowed at proper temperatures. Whether troostite is the proper term is open to discussion, as it might also he called sorbite or sorbitic pearlite: the structure can in places be resolved. Lamellæ are not, however, to be seen.

1200° furnace 800° 2h. Q: Martensite with accentuated grain boundaries (indicating the beginning of cementite separation).

1200° furnace 750° 1h. Q: Martensite and a network, partly interrupted, of cementite.

[1] This difference is explained by the fact that the cooling rate in this case was much slower: 9° per minute at 750° C. (35° per minute on cooling from 910° C.)

1200° furnace 715° 2h. Q: Martensite and a continuous network of narrow cementite lines; traces of pearlite in the decarbonized surface layer.

1200° furnace 710° 1h. Q: Martensite and a network of cementite; also some rather large areas of pearlite, partly lamellar. This structure is shown on photo No. 16.

1200° furnace 700° 1⅓h. Q: Ill-defined and partly lamellar pearlite is the predominating structure; only small remainders of martensite. The cementite is broken up into separate grains.

1200° furnace 700° 3h. Q: No martensite is present.

The conclusions which may be drawn from the experimental data just related are:

(1) On sufficiently slow cooling from 1200° C. the pearlite transformation occurs at about 715° C. (as compared with about 730° on slow cooling from 910° C.) and possibly somewhat higher on still slower cooling. *The transformation point of the pearlite is not lowered at all, or only slightly so, by a previous heating to 1200° C.*

(2) On cooling from 1200° C. there is a temperature range between about 715 and 600° C. in which the pearlite transformation takes place, and gradually proceeds undisturbed by other transformations, until the austenite is completely decomposed, if sufficient time is allowed.

(3) On cooling from 1200° C. the rate of formation of pearlite in the temperature range mentioned, examined at 715, 710, 700, and 600° C., was found to be greatest at 700° C. and least at 715° C., and is consequently maximum somewhere between 700 and 600° C.

In order to ascertain the most favorable *conditions for the forming of secondary ferrite* the following experiments were made:

1200° furnace 800° 10½h. furnace 910° furnace 650, 600, 550, and 500° Q: The structures were the same as those formed by continuous cooling in the furnace from 1200° and quenching at the same temperatures.

Consequently, after heating to 1200° C. has once taken place, the austenite does not lose the properties thus obtained (slowness in transformation) by being subjected to an extended soaking at 800° C. before the final cooling; that such a soaking at a

temperature below Ar_1 (about 715° C.) results in complete transformation into pearlite is proved by the previous experiments. A similar experiment by Böhler is thus verified.

1200° air 575° 15 mins. Q: The structure is shown in photo No. 17. The main mass consists of coarse-needled martensite and small austenite areas. Inside the pre-existing austenite grains as well as in their boundaries, lines of an unknown constituent are to be seen. A few small troostite grains and mostly in conjunction with these small ferrite grains may be observed.

1200° air about 550° Q: Coarse martensite and small austenite areas.

1200° air 550° 15 mins. Q: The structure is shown on photo No. 18. In the matrix—martensite and austenite—lengthened formations similar to pearlite with ferrite constituent accentuated, are seen and also numerous isolated needles or " streaks " dark in color when etched and often slightly curved or broken; some groups of parallel streaks are found.

1200° air 550° 5h. Q: Small remaining areas of martensite, containing " streaks " and lying in a coarse interwoven mass, which resembles pearlite.

1200° air 525° 15 mins. Q: A coarse structure, resembling pearlite (see the previous one).

1200° air normal temperature: Traces of martensite areas in a pearlite-resembling mass.

The last experiment shows, that *this steel is not self-hardening.*

From the preceding experiments it is apparent that the *secondary ferrite*, which on continuous cooling from 1200° C. is obtained at about 580 to 515° C., and in distinct *Widmannstätten formations*, is *far from stable as to this shape*, since if the specimen is kept at a temperature below 550° C. for about 15 mins., it passes with the remaining austenite into a coarse pearlite-resembling mass.

Furthermore, in these experiments a structural constituent has been found, which for lack of a better name has been termed *streaks*. When etched these streaks appear as straight or bent needles of a dark color inside the grains of the pre-existing austenite and are formed when the specimen is kept for sometime at a temperature of 575 to 550° C. on cooling down from 1200° C.

They are probably slip bands, caused by deformation within the austenite grains. This deformation may be due to the separation of ferrite.

The experiments carried on thus far have had reference to initial temperatures of 910 and 1200° C. These are amplified by the following experiments with the intermediate initial temperatures of 1000 and 1100° C.

Cooling from 1000° and 1100° C.

1000° furnace 675° Q: Martensite.

1000° furnace 650° Q: Pearlite with separate grains of martensite.

1000° furnace 600° Q: Only pearlite.

1100° furnace 675° Q: Martensite.

1100° furnace 650° Q: About one-third of the mass consists of pearlite and the rest of martensite.

1100° furnace 600° Q: In the center the entire mass has now changed to pearlite. Martensite grains still appear in the intermediate zone between center and surface.

1100° furnace 550° Q: In the martensite grains at the intermediate zone now appear distinct Widmannstätten separations of *secondary ferrite.*

In Table II is given a review of the beginning and development of the pearlite transformation as well as the secondary ferrite separation on cooling from different initial temperatures.

From the table is seen that *with increase of initial temperature a change takes place in the course of pearlite transformation on cooling resulting in beginning at lower temperatures and proceeding at a slower rate. As soon as the initial temperature exceeds a certain value, which in this case is about 1100° C., the pearlite transformation proceeds so slowly, that, at this rate of cooling, part of the austenite remains untransformed at about 550° C. This makes it possible for a transformation to occur characteristic of austenite at such low temperatures, viz., the separation of secondary ferrite, which starts at about 550° C. and proceeds at a rate which seems not to be influenced by the height of the initial temperature.*

Before leaving the B_3 steel it seems appropriate to consider the tungsten carbide present in the steel.

TABLE II

Initial Temperature	910° C.	1000° C	1100° C	1200° C
Structure of specimen quenched from	650°	Pearlite only	Largely pearlite	About ¼ pearlite	Trace of pearlite
	600°	.....	Pearlite only	Central portion pearlite only; intm. zone largely pearlite	
	584°	.....	.....	.....	About ¼ pearlite + ¾ martensite
	550°	.....	.....	= the previous one + sec. ferrite in the martensite	
	540°	.....	.....	.....	= the previous one + sec ferrite in the martensite

No attempt has been made to determine the quantity of WC in this steel but it might be assumed to be 0.5 per cent. WC contains 6.12 per cent C and 93.88 per cent W. The total quantities of W and C in 100 g. of steel are according to the assumption made, distributed in the following manner:

WC contains	0.03 g. C and 0.5 g. W.
The matrix contains	0.91 g. C and 2.4 g. W.
Total	0.94 g. C and 2.9 g. W.

The matrix—the austenite—thus contains 0.91 per cent C and 2.4 per cent W. If the solubility of WC in austenite is considered as approximately constant, it is clear that so far as the position of the transformation points and the rate of transformation are concerned, the B3 steel acts the same way as a steel of the composition C = 0.91 per cent, W = 2.4 per cent. In this respect the remaining 0.03 per cent C and 0.5 per cent W are consequently of no account.

The amount of WC in this steel is not great, wherefore its influence in reducing the C and W contents of the austenite is

small. It is evidently necessary, however, in studying the influence of different C and W contents on the transformations of tungsten steels, to take into consideration that the presence of free carbide of tungsten will reduce the concentration of C and W in the matrix.

Steel B5; C=1.29 Per Cent, W=4.8 Per Cent

In the annealed state, this steel consists of granular pearlite similar to that of steel B3.[1]

When hardened, irrespective whether from a low or high temperature, a considerable amount of WC appears, usually in the form of angular grains which always stand out in relief. On polishing these grains are liable to cause scratches in the surface of the specimen. Examined by the eye the polished steel surface appears dull, as if it were etched.

The structure of this steel quenched at 1200° C. is illustrated in photos Nos. 19 and 20, the magnification being 500 and 1200 diameters respectively. The matrix is composed of coarse martensite needles alternating with austenite areas. It will be noted that the surfaces of the carbide grains are round instead of flat, an indication of their hardness.

Cooling experiments from 1200° C., similar to those with steel B3, were carried out, the specimens being allowed to cool in the furnace. The results were as follows (WC, always being present, is not mentioned).

1200° furnace 750° Q: Coarse-needled martensite with a continuous network of thin cementite lines.

1200° furnace 650° Q: Martensite and increased quantities of cementite now broken up into separate grains; a considerable amount of *troostite* has formed (about half the mass). In the decarbonized surface layer no troostite is present, but some primary ferrite is visible at the edge of the specimen.

The corresponding experiments with steel B3 showed only slight troostite formation.

1200° furnace 600° Q: The troostite has increased to such an extent that only traces of martensite are left in the central

[1] WC, which is present, is hard to detect in this structure.

portions. As the surface is approached the troostite decreases as well as the cementite. In the surface layer only martensite and separated primary ferrite appear.

1200° furnace 550° Q: The troostite transformation is now complete in the central portion. The gradual decrease in troostite towards the surface is to be seen from the photos Nos. 21, 22 and 23, which show the structure in the center and at a depth of about 1.5 and 0.5 mm. respectively beneath the surface. All martensite areas contain needles and seams of *secondary ferrite*. In the immediate surface layer no troostite is present, the structure consisting of martensite and separations of *both primary and secondary ferrite* forming partly continuous grains; the latter through its Widmannstätten arrangement may be easily distinguished from the former.

The heterogenous structure of the preceding specimens can hardly be due to the slight difference in the rate of cooling at the center and the surface, but is likely to be caused by different carbon contents due to decarbonization which is rather deep in this steel. This explanation is also based upon the very plausible assumption that the separation of excessive cementite in the central portion was incomplete on account of undercooling.

1200° furnace 500° Q: The secondary ferrite has increased while the troostite remains constant.

The cooling experiments from 1200° C., with steel B5, so far related, when compared with those of steel B3, indicate that in steel B5, the *cementite* is separated earlier and in larger quantities, the *troostite* (pearlite) is formed earlier and in larger quantities, the *secondary ferrite* is separated somewhere in the same temperature range as in steel B3.

The difference with regard to the cementite is natural on account of the higher carbon content in steel B5. The course of the troostite transformation shows that the austenite of steel B5 is more easily decomposed, i.e., is less stable than that of steel B3. This seems unexpected in view of the higher tungsten content of steel B5, but is explained as follows:

The relative stability of the austenite phase is evidently a function, not of the total composition of the steel, but of the composition of the austenite. In order to ascertain this com-

position, the amount of tungsten carbide present was determined in the following manner:

Specimens quenched at 1000° C., wherein all cementite was in a solid solution, were dissolved in dilute sulphuric acid (for further details see p. 59). As an average of two determinations the carbide residue thus obtained amounted to about 3 per cent. The composition of the carbide being WC, the approximate composition of the austenite at 1000° C. is calculated to be 2.0 per cent W, 1.14 per cent C.

The relative stability of the austenite of steel B5 as compared with that of B3 is evidently primarily due to its lower tungsten content, but must also be ascribed to the higher carbon content, this latter influence being indicated as well in the decarbonized specimens mentioned above. The assumption is still held that the separation of excessive cementite is incomplete on account of undercooling just as the pearlite transformation is found to be incomplete.

In other words, the steel B5, in spite of its composition of 4.8 per cent W and 1.29 per cent C, as regards transformation qualities, acts like a steel with 2.0 per cent W and 1.14 per cent C, the remaining 2.8 per cent W and 0.15 per cent C forming the tungsten carbide.

As with steel B3, a series of cooling experiments were carried out, the cooling (in the furnace) being checked at a certain temperature, and this temperature kept constant for a fixed period, after which the specimen was quenched. Briefly the following results were obtained:

On Slow Cooling: Cementite begins to separate in large quantities forming a thick network, at a temperature between 900 and 800° C.

Pearlite is formed: in the decarbonized surface layer at a temperature slightly above 725° C.; in the center at a temperature slightly above 715° C.

The following *air cooling experiments* were also made:

1200° air 575° 15 min. Q: Martensite and a thin network of *cementite.* In addition a large number of *streaks* appear inside the martensite grains. In a ring-shaped zone around the center, traces of *troostite* are seen.

That the center itself is free from troostite is most probably due to the fact that the contents of W, P, etc., are greater here owing to segregation during solidification.

1200° air 550° 15 mins. Q: Small grains of *secondary ferrite* have separated in the center as shown by photo No. 24. Close to the surface appear needles of *secondary ferrite* in large quantities; otherwise the structure is similar to the previous one.

1200° air 525° 15 mins. Q: The structure of the center, magnified to 500 and 1200 diameters respectively, is shown in photos Nos. 25 and 26. The ferrite has increased but a ring-shaped zone a little beneath the surface is free from ferrite. As may be seen from photos Nos. 25 and 26 the ferrite grains have partly an irregular and partly a lengthened shape. Otherwise the same structure is found as in the previous specimen, and particularly as regards streaks.

1200° air 500° 15 mins. Q: The appearance is shown on photo No. 27. The structure is now entirely changed and consists of a main mass similar to pearlite in which small areas of martensite are embedded.

1200° air-normal temperature: This is similar to the previous one.

These air-cooling experiments from 1200° C. show that, when the air cooling is interrupted at a certain temperature and this is kept constant for fifteen minutes:

(1) *Secondary ferrite* is separated at 550 and 525° C. but not at 575° C.;

(2) *Cementite and streaks* are formed at 575, 550 and 525° C.;

(3) *A Pearlite-resembling* mass appears at 500° and lower temperature.

The first three constituents thus formed appear isolated from each other.

Reviewing steel B5 it might be said that it has properties similar to steel B3 in regard to:

Cementite separation;
Pearlite transformation at different rate of cooling;
Secondary ferrite separation;
Formation of streaks, and
The rapid decomposition of austenite at about 500° C.

The differences in degree noticed in these phenomena, comparing steel B3 and steel B5, are explained by the difference in composition of the austenite phases. This composition differs more from the total composition in the case of steel B5 than of steel B3, on account of the considerably greater amount of tungsten carbide present.

Steel B1; C = 0.75 Per Cent, W = 1.6 Per Cent

The structure of this steel, when annealed, is granular pearlite; when hardened, martensite. No WC is found.

The following continuous cooling experiments were made:

1200° furnace 650° Q: Pure martensite.

1200° furnace 600° Q: Martensite and some *troostite* just below the surface.

1200° furnace 550° Q: In the central portion troostite or pearlite and some areas of martensite containing *streaks;* as the surface is approached the martensite areas increase and are found to contain *secondary ferrite* in the usual arrangement, in addition to the streaks.

The following experiments with checked cooling were made:

1200° furnace 705° 3h. Q: Pure martensite.

900° furnace 715° 2h. Q: Martensite and a few small grains of *ferrite.*

The steel B1 consequently has the following characteristics:

It contains no tungsten carbide;

Has hypo-eutectoid composition;

Secondary ferrite is separated at about 550° C. on cooling from 1200° C.;

Its stability is comparable with that of steel B5.

Steel B2; C = 0.95 Per Cent, W = 0.95 Per Cent

When annealed the steel consists of granular pearlite, when hardened, of martensite in which, on close examination, a few minute grains of WC were detected.

The following experiments were made:

1200° furnace 650° Q: Martensite.

1200° furnace 600° Q: Pearlite only.

1200° furnace 800° 2h. Q. Martensite.

1200° furnace 750° 1h. Q. Martensite.

1200° furnace 715° 2h. Q. Martensite and cementite, separated in the austenite boundaries, as shown by photo No. 28

1200° furnace 705° 3h Q. Similar to previous specimen.

The characteristics of steel B2 can be summed up as follows:

It contains a minute amount of WC,

Has a hyper-eutectoid composition, and

Has the least stability of the steels so far investigated, for which reason the austenite, on cooling from 1200° C. in the furnace, transforms entirely into pearlite, before that temperature range is reached where secondary ferrite is separated. This is to be expected in view of the low tungsten content and relatively high carbon content.

The steels B3, B5, B1, and B2, so far investigated may be considered as tool steels. The following steel No. 6 has a composition typical of magnet steels.

Steel No. 6; C=0.61 Per Cent, W=6.4 Per Cent

In the untreated condition this steel has an irresoluble pearlitic or sorbitic structure. After hardening a number of round white grains appear embedded in the martensitic matrix. These grains do not stand out in the high relief, characteristic of WC grains, have flat surfaces and are consequently more similar to cementite as to hardness. When etched with boiling sodium picrate they are rapidly colored brown or black. On heat tinting they color faster than WC but more slowly than cementite (this has been definitely ascertained in specimens containing all three carbides; see later discussion).

Their composition has not been determined in this investigation, but several reasons, to be given later on, make it seem probable that they consist of a *double carbide of iron and tungsten*. Photo No. 29 depicts a specimen of this steel hardened at 1200° C. and heat tinted to show the white double carbide in the dark matrix.

Probably this carbide is more soluble in the austenite at higher temperature. No evidence for this, however, is found in the microscopic examination of specimens of this steel, hard-

ened at different temperatures up to 1200° C. It appears in all specimens of steel No. 6, no matter to what heat treatment they have been subjected. No mention, is therefore, made of it in dealing with the structures of the specimens.

Experiments made with this steel discussed in the following concern the following phenomena and characteristics:

(1) The relative stability of the austenite on ordinary cooling in the furnace from 1200 and 850° respectively;

(2) The position of Ar_1 on very slow cooling from 1200° C. and the rate of pearlite transformation, and

(3) The separation of secondary ferrite and formation of streaks.

(1) THE STABILITY OF THE AUSTENITE

1200° furnace 600° Q: Martensite and a small quantity of thin formations in the grain boundaries, probably consisting of troostite (see photo No. 30).

1200° furnace 550° Q: In the martensite appears the beginning of a minute separation, not possible of identification (see the following specimen). The troostite has not increased.

1200° furnace 500° Q: The structure may be seen from photo No. 31. As will be noticed, *secondary ferrite* has separated in large quantities, partly associated with the network of troostite already existent and partly inside the austenite grains in Widmannstätten arrangement.

1200° furnace 450° Q: The structure is shown in photo No. 32. The secondary ferrite has now still further increased. The matrix is partly martensitic and has partly decomposed into dark areas.

850° furnace 650° Q: Pearlite (sorbitic) alone.

Summing up these results, it may be stated, that steel No. 6:

When cooled from 1200° shows slight troostite formation somewhere above 600° C., and a considerable separation of secondary ferrite, starting at about 550° or somewhat lower and continuing below 500° C.;

When cooled from 850° C. is entirely transformed into pearlite above 650° C.

Consequently the austenite of this steel, when cooled from high temperature has a considerably greater stability than those of the steels previously investigated and when cooled from lower temperatures (still above Ac_1) quickly transforms into pearlite as the others do.

(2) PEARLITE TRANSFORMATION

1200° furnace 750° 2h. Q: See photo No. 33. The main mass consists of coarse-needled martensite. In the grain boundaries thin continuous formations are seen, which do not resemble ferrite, but must be assumed to be *pearlite* (or troostite or sorbite) which assumption is verified by the following experiments:

1200° furnace 730° 2h. Q: See photo No. 34. The pearlite has now increased.

1200° furnace 730° 2h. furnace 715° 2h. Q: See photo No. 35. The pearlite has increased still more and now occupies about half of the surface.

1200° furnace 730° 2h. furnace 715° 2h. furnace 700° 2h. Q: Pearlite and small areas of martensite.

1200° furnace 730° 2h. furnace 715° 2 h. furnace 700° 2h. furnace 685° 2h. Q: Similar to the previous specimen.

These experiments show that, on very slow cooling from 1200° C.:

No separation of free ferrite or cementite is noticeable; from which can be inferred that this steel has eutectoid composition and

That the pearlite transformation starts slightly above 750° C. and proceeds very slowly so that after cooling for eight hours from 730 to 685° C., it was not quite completed.

(3) SECONDARY FERRITE, ETC.

1200° air 600° ½h. Q: See photo No. 36. Martensite with distinct grain boundaries, probably indicating a minute troostite formation; a few small troostite patches appear.

1200° air 600° 5h. Q: See photo No. 37. The troostite or pearlite has increased and is clearly seen but occupies a minor part of the surface in spite of the long pause at 600° C

1200° air 550° 15 mins. Q: Martensite only.

1200° air 525° 1 min. Q: Martensite and clearly visible separations of *secondary ferrite* of usual appearance.

1200° air 525° 5 mins. Q: An increased quantity of secondary ferrite.

1200° air 525° 15 mins. Q: Considerable ferrite separation (see photo No. 38).

1200° air 500° 15 mins. Q: The amount of ferrite is larger than in the previous specimen.

1200° air 500° 1½h. Q: The ferrite has increased still more; in the martensite a number of *streaks* are visible.

1200° air 475° 1½h. Q: The secondary ferrite now occupies such a large space, that the solid solution remaining has the shape of thin needles. It is estimated that the ferrite occupies about two-thirds of the mass. At a low magnification the structure can easily be mistaken for martensite only.

1200° air normal temperature: Martensite and needles of troostite. See photo No. 39.

The above experimental results show that the separation of secondary ferrite takes place very rapidly in the proper temperature range, in comparison with the formation of pearlite. At 600° C., only a small part of the austenite transforms into pearlite even in a period as long as five hours. At 525° C. one minute is sufficient for ferrite to appear, while at 550° C. no ferrite appears in fifteen minutes.

The conclusion is that ferrite begins to separate at 550 to 525° C. and increases in quantity as the temperature falls or the annealing period at a constant temperature is lengthened at least within a certain limit. There is probably an equilibrium corresponding to each temperature.

That the temperature range of ferrite separation upwards is so sharply limited at 550 to 525° C., may be explained as follows: since the pearlite transformation is suppressed, the usual equilibrium diagram cannot be applied but the lines representing the composition at different temperatures of austenite being in equilibrium with ferrite as well as with cementite should be extended to lower temperatures as shown sketched in Fig. 3*a*.

As soon as the specimen in cooling has passed about 750° C.,

the austenite is undercooled with regard to ferrite as well as to cementite; their crystallization power [1] is, however, through the stabilizing heating, reduced to such a degree that no separation or pearlite transformation takes place at the cooling rate applied, While the crystallization power of cementite has only one maximum at about 700° C., and below this decreases with falling temperature, the ferrite has, besides this upper maximum, a lower, distinct maximum at 525° to 475° C. (see Fig. 3*b*). The con-

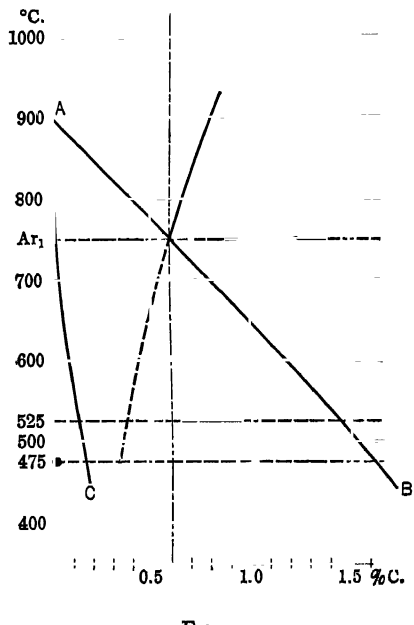


FIG. 3*a*.

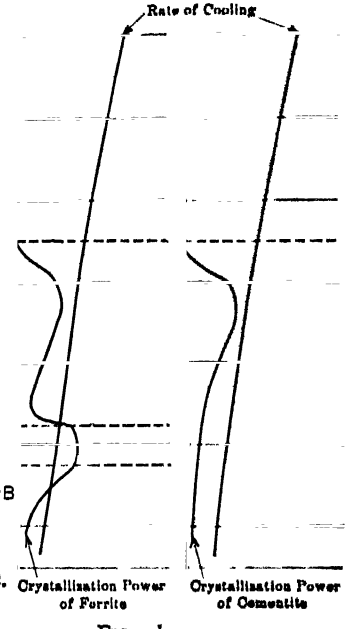


FIG. 3*b*.

sequence is that at this temperature ferrite only is separated and this takes place in such quantity that the composition of the remaining austenite changes towards a higher carbon content, until the extended equilibrium line AB (see Fig. 3*a*) is reached provided sufficient time is allowed. The composition of the separated ferrite follows the extended equilibrium line AC,[2]

[1] This expression is used in the sense of including the number of nuclei of crystallization formed per time unit as well as the linear growing rate.

[2] This diagram being only schematic, the tungsten content is not taken into consideration.

so that this ferrite might be expected to contain another and probably higher carbon content than the ferrite, which is in equilibrium with cementite. On the assumption made, the separated ferrite as well as the remaining austenite are unstable, the former in regard to its composition, the latter as a phase. The quantity of separated ferrite deducted from this diagram is in agreement with the approximate amount, estimated from microscopical examination of specimens exposed for a long period to these temperatures.

Another possible explanation of the secondary ferrite phenomenon is the following: It might be assumed that the separation of ferrite was due to the passing of another equilibrium line lower than AB, viz., the line representing the composition of austenite in equilibrium with β-iron, extended out to lower temperatures; the β-ferrite then assumed to possess a greater crystallization power than α-ferrite. In order to study this hypothesis the following experiments were made:

1200° air 550° furnace 500° 15 mins. Q: Martensite and ferrite as usual.

1200° air 550° furnace 500° 15 mins. furnace 600° 15 mins. Q: Martensite and ferrite as in the previous specimen. In the martensite isolated patches of troostite are also found.

1200° air 550° furnace 500° 15 mins., furnace 600° 2 hrs. 15 mins. Q: The quantity of ferrite has *increased* somewhat, as well as the quantity of troostite; otherwise similar to the previous one.

If the ferrite separation were caused by the passing of the equilibrium line of austenite toward β-iron, it might be expected that the separated ferrite ought to dissolve in the austenite again on reheating above the same line. This was, however, not the case. These experiments are mentioned for the value they may have.

A. C = 0.47 Per Cent. W = 4.1 Per Cent

This steel was produced by melting together alloy K (C = 0.30 per cent, W = 28.3 per cent; see later) with carbon steel (C = 0.65 per cent) in an electric furnace, system Hanemann (granular carbon resistance). The weight of the melt was about 50 g.

It had a distinct hypo-eutectoid composition and lacked free carbide.

Since the melt contained rather many blowholes and on microscopical examination proved to be of a somewhat heterogeneous composition, only the following experiments will be mentioned:

Specimens cooled from 1200° C. in the furnace were quenched at different temperatures. It was then found that ferrite in the form of network—*primary ferrite*—was separated at a temperature above 650° C., and *secondary ferrite* in usual arrangement started separation between 600° and 550° C.

Experiments with checked cooling gave the following results: 1200° furnace 750° ½h. Q: Martensite and *primary ferrite* as shown by photo No. 40.

1200° air 625° 10 mins. Q: Martensite without any separations. See photo No. 41.

1200° air 575° 10 mins. Q: Martensite and distinct separations of *secondary ferrite* in Widmannstätten arrangement. See photo No. 42.

Consequently in this steel also, on cooling from 1200° C. *secondary ferrite* is separated below a certain temperature, about 600° C., while at a temperature just above this there is no such separation. At a higher temperature, about 750° C., on the other hand, *primary ferrite* is separated just as in carbon steels, on account of the hypo-eutectoid composition of the steel. For a comparison of these two kinds of ferrite in regard to shape and arrangement see photos Nos. 40 and 42.

C. DISCUSSION OF THE RESULTS OBTAINED

The results obtained in the previous investigation make possible a general view of the transformation qualities of tungsten steels containing less than about 7 per cent tungsten.

(1) Presence of Free Carbide and Composition of the Austenite

The transformation properties of a tungsten steel depend on the composition of the austenite phase and not on the total composition of the steel, these two compositions being identical only when no free carbide is present.

Free carbide was found in some of the steels investigated as shown by Table III, in which the steels are arranged according to the total tungsten content.

TABLE III

Steel Marked.	C Per Cent.	W Per Cent.	Carbide.		Austenite Composition.		Hypo- or Hyper-Eutectoid.
			Composition.	Amount.	C Per Cent.	W Per Cent.	
B2	0.95	0.95	WC	Traces	<0.95	<0.95	Hyper-eutectoid
B1	0.75	1.6	... ..	.. ..	0.75	1.6	Hypo-eutectoid
B3	0.94	2.9	WC	Slight	About 0 91	About 2.4	Hyper-eutectoid
A	0.47	4.1	.....	... ..	0 47	4 1	Hypo-eutectoid
B5	1.29	4.8	WC	About 3%	About 1.14	About 2 0	Hyper-eutectoid
6	0.61	6.4	Double carbide	Slight	<0.61	<6.4	Eutectoid

From Table III it will be seen that for a given tungsten content the solubility of carbon in the austenite is limited to a certain carbon content. As soon as this is exceeded, free carbide appears, either WC or double carbide (see section II). In other words, *if the carbon content is high, the tungsten content of the austenite will be considerably reduced and the transformation characteristics of the steel will be the same as those of a steel of lower percentage of tungsten and carbon.*

Although it ought to be expected that the carbide present—WC or double carbide—has a greater solubility in austenite at higher temperature, just as cementite, no sign thereof has been found in the microscopical investigation made. The carbide was in no case brought into complete solution at 1200° C. The cementite present in hyper-eutectoid steel was found to dissolve on heating and separate on cooling as in carbon steels.

(2) The Eutectoid Composition at Different Tungsten Contents

The properties of the steels investigated, in this respect, are also given in Table III. From the table may be inferred that *tungsten content displaces the eutectoid composition toward lower*

carbon content. Approximately 6 per cent tungsten [1] and 0.6 per cent carbon [1] form eutectoid composition.

One per cent tungsten seems to reduce the eutectoid carbon content about 0.05 per cent.

(3) The Position of the Pearlite Transformation Temperature on Very Slow Cooling at Different Tungsten Contents

The results obtained in experiments with checked cooling are compiled in Table IV, the steels being arranged according to increasing tungsten content in the austenite phase.

TABLE IV

Steel Marked.	Total.		Composition of the Austenite.		Beginning of Pearlite Transformation at Very Slow Cooling from	
	C Per Cent.	W Per Cent	C Per Cent.	W Per Cent.	910° C	1200° C.
B2	0.95	0.95	0.95	0.95		$<705°$
B1	0.75	1.6	0.75	1.6	$<715°$	$<705°$
B5	1 29	4.8	About 1.14	About 2.0	...	$>715°$
B3	0.94	2.9	About 0.91	About 2.4	$>725°$	About 715°
6	0 61	6.4	<0.61	<6.4		$>750°$

From the table it will be seen that the pearlite transformation point is raised by tungsten. Although the temperatures given are not quite exact (due to the difficulty of regulating the furnace at a constant temperature for an extended period), it may be estimated that 1 *per cent tungsten in the austenite raises the pearlite transformation point* Ar_1 *on very slow cooling with about* 10° *C.*

In addition, it should be pointed out, that the position of Ar_1 in tungsten steel is a function not only of the tungsten content dissolved in the austenite, but also of the dissolved carbon content, since it is *a priori* probable, that free ferrite or cementite separated before the pearlite transformation (in hypo- or hypereutectoid steels) contains tungsten in another percentage than that of the austenite and consequently on separation displaces the tungsten content of the austenite in one direction or the

[1] The approximate austenite composition of steel No. 6.

other. Experiments with retarded cooling made on steel of the same tungsten content and different carbon contents would solve this question.

By heating to a high temperature the position of Ar_1 on very slow cooling is not affected (or possibly slightly lowered) (See B_3 in Table IV.).

(4) Effect of Heating to a High Temperature before Cooling

(*a*) The experiments with heating to 910, 1000, 1100, and 1200° C. have shown that *at least within certain limits with increasing temperature the austenite phase changes in a direction of greater stability, i.e., transformations of this phase occurring at an ordinary rate of cooling, start at a lower temperature and proceed more slowly.*

This is accentuated by higher tungsten content dissolved in the austenite and by quicker cooling.

Probably *higher dissolved carbon content* acts in the opposite manner.

Dependent on the degree of stabilization the pearlite transformation on ordinary cooling may either fail to occur or may set in at separate points in the mass and, slowly proceeding, stop before completion on account of a temperature being reached in the meantime, where the rate of pearlite transformation is negligible. This temperature seems to be about 600° C.

The stabilized state of the austenite is unchanged by soaking for ten hours at a temperature somewhat above A_1 (i.e., Ar_1 on very slow cooling). If, on the other hand, the stabilized steel is cooled to such a temperature (below Ar_1), that the pearlite transformation occurs and sufficient time is given for its completion, and the steel is then reheated above Ac_1, e.g., to 900° C., a subsequent cooling will show, that the stabilized state is lost. The new austenite, formed at Ac_1, will quickly transform into pearlite on cooling.

The theoretical explanation of the stabilization phenomenon is not revealed by the present investigation. It cannot, however, be ascribed to free carbide, being dissolved in the austenite on heating to a high temperature, since stabilization is found to occur even in steel without free carbide.

A result of the stabilization is that the austenite at a tungsten content exceeding 1 per cent either partly or entirely remains, when the cooling reaches lower temperatures, which is not the case in the cooling of carbon steels (except in rapid cooling). This austenite, therefore, is subject to other kinds of transformation, characteristic of these low temperatures. Such a transformation is the following:

(*b*) *Separation of Secondary Ferrite.*

If a stabilized tungsten steel is allowed to cool at a normal rate in a furnace, a separation of ferrite, called secondary ferrite, from the untransformed parts of the austenite starts at a temperature between 600 and 525° C. the ferrite increasing on continued cooling.

The secondary ferrite appears partly as seams in the boundaries of the austenite grains or existing troostite areas and partly as needles arranged in the cleavage planes of the austenite grains; thus a Widmannstätten structure is formed similar to the appearance of ferrite separations in hypo-eutectoid carbon steels, overheated and not too slowly cooled.

The crystallization power of the ferrite in this temperature range is rather high compared with the rate of pearlite transformation in a stabilized steel (see Fig. 3*b*), for which reason secondary ferrite is always found in a tungsten steel normally cooled from a high temperature. Air cooling is, however, sufficient to suppress its separation in small specimens.

The upper temperature limit of secondary ferrite separation in different steels is seen from Table V.

TABLE V

Steel Marked.	Composition of Austenite.		Highest Temperature of Secondary Ferrite Separation Found. °C.
	C Per Cent.	W Per Cent.	
B1	0.75	1.6	Between 600 and 550
B5	About 1.11	About 2.0	Between 600 and 550
B3	0.91	2.4	About 575
6	<0.61	<6 4	Between 550 and 525

This temperature is lowered by higher tungsten content and probably by higher carbon content, but as a whole is affected to a small extent by the composition of the austenite.

The ferrite separation is caused by an increase in crystallization power of the ferrite in this temperature range.

A consequence of the ferrite separation is that the carbon content of the austenite is increased, possibly to about 1.5 per cent. The ferrite itself has probably a higher carbon content than the common kind of ferrite, partly because it is in equilibrium with austenite—not with cementite—and, partly because its formation temperature is low (see Fig. 3*a*).

(*c*) In the same temperature range in which the secondary ferrite is separated an unknown constituent is also formed in the austenite called *streaks*, in the shape of thin needles in Widmanstätten arrangement, which appear dark after etching. The streaks, however, require a longer time for their formation than the secondary ferrite does. The streaks may be slip bands, formed within the austenite grains as a result of deformation, caused by the ferrite separation. This conclusion is borne out by the fact, that when steel No. 6 in cooling from 1200° C. was kept for five hours at 600° C. neither secondary ferrite nor streaks were formed.

(*d*) When the stabilized austenite on cooling reaches 500 to 450°, at least at moderate tungsten contents, it decomposes into a pearlite-resembling mass; this is the case as well when the secondary ferrite separation has occurred as when it has been suppressed by quick cooling through its formation range.

(*e*) In all quenched specimens which contained austenite before quenching, this has been found to consist of martensite after quenching except in some cases, where small austenite areas are left. This applies to all quenching temperatures from 1200 to 500° C. From this fact it must be concluded that *the martensite is formed at a lower temperature than* 500° C. *and at a rapid rate.*

(*f*) *The form of the cooling curve in cooling from high temperatures.*

From the discussions above it may be concluded, that in the cooling curve of a stabilized tungsten steel, critical temperatures and temperature ranges corresponding to the following transformations may be seen:

(1) *Separation of excessive ferrite or cementite* (in hypo- or hyper-eutectoid steel).

(2) *Pearlite transformation*, usually not complete, starting at a lowered temperature and finishing about 600° C.

(3) *Secondary ferrite separation* from the remaining austenite starting somewhere between 600 and 525°, according to the composition, and continuing to about 500° or lower, depending upon whether the following transformation takes place or not.

(4) *The decomposition of remaining austenite*, partly or entirely, to a mass resembling pearlite around 500 to 450° C.

(5) The *transformation of remaining austenite*, partly or entirely *into martensite* at a temperature below the previous one.

The transformations which actually occur and are visible in the cooling curve depend on the following factors:

Tungsten content; Carbon content; Initial temperature and time allowed at this temperature; Rate of cooling.

If for the sake of simplicity, tungsten steels of eutectoid composition are taken as examples, high tungsten content as well as quick cooling, will lower and reduce, possibly even eliminate the pearlite point (2).

The occurrence of the secondary ferrite point, often called the lower recalescence point, depends in cooling from high temperature chiefly on the rate of cooling. A necessary condition is evidently that at least a part of the austenite is left at this temperature range, for which reason the secondary ferrite point also depends in an indirect way on the other factors mentioned.

D. CRITICAL DISCUSSION OF PREVIOUS INVESTIGATIONS [1]

(1) *The gradual lowering and decrease in magnitude of* Ar_1 *on cooling from increasingly high initial temperatures*, were, by Böhler, Guillet and Swinden, ascribed to a real lowering of the pearlite transformation point and not to a decrease in the rate of pearlite transformation. As seen from the author's experiments, the latter explanation is the correct one, since the pearlite transformation, on sufficiently slow cooling takes place without lowering. This view was also adopted by Osmond if the author understands him rightly, and by Carpenter as well.

[1] Literature references are found in section 1–A.

(2) The lower critical point which appears on cooling from sufficiently high initial temperature has been the object of several different hypotheses.

Osmond considered it to correspond to a pearlite transformation, occurring in certain parts of the mass, in which, on heating, the cementite (pearlite?) was more completely dissolved than in other parts.

Böhler understood the lower point to signify a pearlitic transformation, as well as the upper one.

According to Swinden Fe_3W present in the steel is dissolved at the high ("lowering") temperature and in this solution Fe_3C is then dissolved. At the lower point both are separated.

Both Osmond and Swinden speak of the pearlite transformation as if it were only a cementite separation and not a transformation of the austenite into two new phases—ferrite and cementite.

Edwards looks upon the lower point as being the critical point of a special carbide of tungsten, formed at 1200° C.

According to Dejean it is simply the transformation of austenite into martensite, which takes place at the lower point, this being found in all kinds of alloy steel.

In the author's experiments with normal cooling from high temperature of steels with a tungsten content from 1.6 to 6.4 per cent a considerable amount of ferrite has been found to separate in a temperature range corresponding to the lower critical point, found by all investigators. Consequently there seems to remain no doubt that the lower point is due to separation of ferrite.

That the martensite formation may appear as a critical point in the cooling curve, will not be denied, but martensite formation not preceded by ferrite separation, seems, according to the author's results, possible only at fairly quick cooling. Consequently Dejean's hypothesis does not cover the lower point phenomenon. It is possible, also, that secondary ferrite, forming a Widmannstätten structure in martensite, was mistaken by Dejean for martensite.

For the hypotheses of Swinden and Edwards no experimental evidence has been given.

To consider the lower point as a second pearlite transformation (Osmond and also Böhler) implies an overlooking of the secondary ferrite, which is easily done if specimens cooled to normal temperature in the furnace are the only ones examined. In the author's experiments a decomposition of the austenite was also found at about 500° C. or lower temperature, which might be considered as a second pearlite transformation, but this was always preceded by a distinct ferrite separation.

The temperature of the beginning of the ferrite separation was found to be between 600 and 525° C., which well agrees with the lower point found by other investigators.

It should be mentioned here, however, that secondary ferrite probably has been observed before by other investigators, without being recognized, as may be realized from the following cases:

Guillet noted in a steel, annealed at 900° C. for four hours and then slowly cooled, that the pearlite had Widmannstätten arrangement. The steel had the following composition: 0.83 per cent C., 4.68 per cent W.

Swinden found in a steel with 1.24 per cent C and 3.02 per cent W, cooled from 1200–1230 to 630° C. during one hour twenty-eight minutes, and then hardened, a peculiar "herring-bone-structure," undoubtedly to be ascribed to the presence of secondary ferrite.

(3) The eutectoid composition is, according to Swinden, not changed by the tungsten content. The author's experiments, on the contrary, seem to indicate, that tungsten displaces the eutectoid composition toward lower carbon content. The amount of displacement given, 0.05 per cent C for each per cent W, is, however, approximate and should be verified by further investigation.

II. CARBIDES IN TUNGSTEN STEELS

A. PREVIOUS INVESTIGATIONS

A. Moissan, 1896.[1] In melting tungstic acid with excess carbon in Moissan's electric furnace, a carbide was obtained of the formula W_2C. The carbide has an iron-gray color and scratches corundum. Its specific gravity is 16.06. When molten it dissolves carbon, which is separated as graphite on cooling.

P. Williams, 1898.[2] 120 g. tungstic acid, 20 g. petroleum coke and 150 g. iron were melted together. The cooled melt was crushed, the magnetic constituents were extracted by magnet and the graphite by washing; the rest was found to be the carbide WC in the form of opaque cubic crystals. The carbide scratches quartz and has a specific gravity of 15.7.

P. Williams, 1898.[3] A product obtained by melting 150 g. tungsten acid, 80 g. petroleum coke and 250 g. iron, was broken up in the manner described above. On treating the magnetic powder thus obtained with aqua regia or boiling hydrochloric acid the residue was found to be a double carbide of the formula $2Fe_3C$, $3W_2C$ in the form of crystals resembling pyrite. The double carbide scratches glass, but not rock crystal, and has a specific gravity of 13.4.

Besides this, the melt contained WC, probably W_2C and several compounds, containing tungsten and iron. The double carbides were magnetic, the tungsten carbides nonmagnetic.

Carnot and Goutal, 1899,[4] dissolved tungsten steels of different composition in acid, obtaining as a residue:

From steel with 0.4–0.6 per cent C, 6 per cent W:	Fe_3W
From steel with 2.0 per cent C., 6.1 per cent W:	$Fe_3C \cdot WC$
From steel with 2.2 per cent C., 7.8 per cent W:	$Fe_3C \cdot WC$

[1] Comptes rendus, 123, p. 123.
[2] Comptes rendus, 126, p. 1722.
[3] Comptes rendus, 127, p. 410.
[4] Comptes rendus, 128, p. 208.

L. Guillet, 1904,[1] investigated tungsten steels of different tungsten content, in two series, one with about 0.2 per cent C the other about 0.7 per cent C. He found on microscopic examination that carbide (double carbide) appeared, when the tungsten content exceeded a certain limit, the position of which depended on the carbon content as seen from Fig. 4.

Guillet stated that this constituent must be a carbide, since it increased in quantity by carburization and was found in steels with lower carbon content, when the tungsten content was higher.

In hardened steels the carbide was found to decrease at higher hardening temperatures. According to Guillet, the carbide consequently should disappear by hardening the steel from high temperature and cooling it rapidly in quenching.

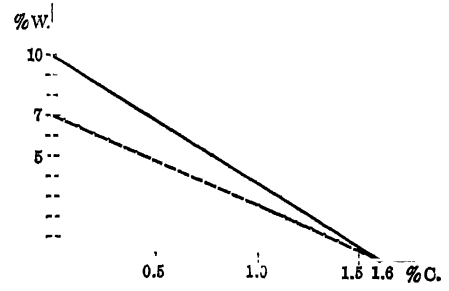


FIG. 4.

At higher tungsten contents the carbide grains had less distinct contours.

Th. Swinden, 1907.[2] A definite Fe-W compound of the formula Fe_3W was obtained in melting together the two metals in the proper proportion.

H. Harkort, 1907[3] investigated Fe-W-alloys with low carbon content and found in the microscope a hard constituent together with ferrite. It seemed to increase with the tungsten content.

S. Hilpert and M. Ornstein, 1913[4] treated fine-powdered

[1] "Aciers au tungstène," Revue de Métallurgie, 1904, p. 263.

[2] "Carbon-tungsten Steels," The Journ. of the I. a. St. Inst., 1907, I, p. 291.

[3] "Beitrag zum Studium des Systems Fe–W," Metallurgie, Nos. 18–20.

[4] "Ueber eine einfache Darstellung von Molybdän- und Wolframcarbiden," Berichte der deutschen Chemischen Gesellschaft, 1913, p. 1669.

tungsten or tungstic acid at high temperature with carbonaceous gases.

At 1000° C. the tungsten or oxide was transformed to W_3C_4 by CO, and at 800° to WC by a mixture of CH_4 and H_2 in the proportion 1 : 1.

O. Ruff and R. Wunsch, 1914,[1] produced in an electric furnace tungsten-carbon and iron-tungsten-carbon melts.

In the tungsten-carbon melts the presence of WC was found through chemical separation and W_3C with metallographical methods; the former at higher, the latter at lower carbon content in the melt. Furthermore, W_2C was supposed to be present in melts of certain compositions.

From the iron-tungsten-carbon melts WC was chemically separated, easiest from melts with low tungsten content, and proved to be identical with the carbide found by Williams.

Ruff and Wunsch doubt the homogeneity of the carbide W_2C, found by Moissan.

J. O. Arnold and A. A. Read[2] investigated a series of steels with about 0.7 per cent carbon and different tungsten contents, from 2.36 to 26.29 per cent.

Annealed samples were electrolytically dissolved in dilute hydrochloric acid. The residues were analyzed. The following conclusions were made:

(1) At a low tungsten content the steel contains iron pearlite just like ordinary carbon steels.

(2) As the tungsten content increases the iron cementite Fe_3C is gradually displaced by tungsten cementite WC, which forms tungsten pearlite. This displacing is completed at 11 per cent tungsten, when no iron cementite is left.

(3) When the tungsten content exceeds 11 per cent, iron tungstide, Fe_2W, appears beside the tungsten cementite.

(4) At high tungsten contents the tungsten cementite in the tungsten pearlite is segregated into isolated larger grains of tungsten cementite.

[1] "Arbeiten im Gebiet hoher Temperaturen III Wolfram und Kohlenstoff," Zeitschrift für anorganische Chemie, 1914, p. 292.

[2] "The Chemical and Mechanical Relations of Iron, Tungsten, Nickel and Carbon," Engineering, 1914, p. 433.

(5) Tungsten forms no double carbide. Numerous attempts with different reagents were made to separate the tungstide and the carbide from each other, but without success.

As seen from the summary made, the presence of the following chemical compounds has been stated in tungsten steels, tungsten-carbon and iron-tungsten-carbon alloys by different investigators.

W_3C, Ruff and Wunsch.

W_2C, Moissan (Ruff and Wunsch).

WC, Williams, Hilpert and Ornstein, Ruff and Wunsch, Arnold and Read.

W_3C_4, Hilpert and Ornstein.

$2Fe_3C \cdot 3W_2C$, Williams.

$Fe_3C \cdot WC$, Carnot and Goutal.

Fe_3W, Carnot and Goutal, Swinden.

Fe_2W, Arnold and Read.

Among these the following were found in steels:

WC, $Fe_3C \cdot WC$, Fe_3W and Fe_2W.

B. THE AUTHOR'S INVESTIGATIONS

(1) PRELIMINARY DISCUSSION

As already has been stated in section I the author in the microscopical examination of tungsten steels, found besides cementite, two carbides or carbide-resembling constituents with the following characteristics:

(1) Very hard, gray-white, not darkened by boiling sodium picrate, very resistant to heat tinting. This constituent which will temporarily be called *X carbide*, was later determined to be WC.

(2) Rather hard (comparable with cementite), is darkened by boiling sodium picrate and is affected more quickly by heat tinting than X carbide. This constituent will be called *Z carbide*.

Table VI shows the characteristics of the steels examined in regard to free carbide present.

TABLE VI

Steel Mark.	Composition. C Per Cent	Composition. W Per Cent.	Carbide.	Amount of Carbide.
B2	0.95	0 95	X	Trace
B1	0.75	1 6		
B3	0.94	2 9	X	Small
A	0.47	4 1		
B5	1.29	4.8	X	Rather great
6	0.61	6.4	Z	Small

It is seen that the X constituent appears at higher carbon contents and is absent at lower, and consequently is likely to be a carbide.

Since the Z constituent is absent in A but present in 6, certain minimum contents of carbon and tungsten apparently are required for its presence, for which reason Z also may be assumed to be a carbide.

(2) CARBURIZATION EXPERIMENTS

The observations mentioned above on the carbide contents at different compositions lead to carrying out some experiments with carburization of steel No. 6 with results as follows:

After soaking for one hour in sugar carbon at 1150° C. and subsequent quenching numerous X grains appeared in the carburized surface layer.

After four hours' soaking the following structure appeared:

(1) The Z carbide has increased in the inner portion of the specimen, partly by forming interrupted narrow seams in the austenite[1] grain boundaries (see photo No. 43) and partly by formation of new, angular grains, contrasting with the former rounded grains. As seen from photo No. 44, the angular-shaped and the rounded grains do not coalesce into homogeneous grains when touching each other. With the etching methods used they show, however, the same characteristics. Assuming them to be different phases, they will be called

[1] For the sake of simplicity the term austenite will be used in many cases in this section as representing the iron phase, existent as the matrix in which free carbide is found, irrespective of whether this constituent, originally austenite has partly or entirely transformed into martensite or pearlite.

Z_1 and Z_2, Z_1 being the first mentioned, Z_2 the second. As Z_2 was formed by carburization it is reasonable to assume that it has a higher carbon content than Z_1.

(2) Approaching the surface Z grains occur mixed with newly formed X grains (see photo No. 45) and at the very surface X grains are the only carbide present, all Z grains having disappeared. The X carbide has the characteristic gray-white color and great hardness. Some of the grains have a well-defined crystal shape, in section appearing as long rectangles or triangles (see photos Nos. 45 and 46, the latter photo taken from the edge of the specimen).

No cementite was found in the specimen as seen in heat tinting; as will be proved later, cementite is faster heat tinted than Z carbide.

(3) WELDING EXPERIMENTS

If two metals or alloys are welded together, the fused zone of the welded specimen ought to contain a series of structures representing alloys of intermediate compositions. This method was used as a means of studying the iron-tungsten-carbon diagram.

Tungsten was electrically welded together with different iron-carbon alloys and with pure carbon. The tungsten metal used was a 4-mm. round wire or rod, furnished by an electric lamp manufacturing firm. The iron-carbon alloys used had the following carbon contents: 0.04, 0.90, 1.79, 3.1, 4.1, and 4.6 per cent.

The steel 1.79 per cent C and the three cast irons belonged to a previous investigation of the iron-carbon system by Dr. Hanemann. The cast-iron samples were white on account of having been cast in the form of thin plates in a mold of silver plate, standing in water.

The structure of the welded specimens were as follows:

(a) Tungsten with soft iron 0.04 per cent C.

Fig. 5 shows a longitudinal section of the welded specimen. C and D consist of ferrite. C is faster colored on heat tinting than D, evidently the result of dissolved tungsten content.

The structure of A and B after heat tinting is shown by photos Nos. 47 and 48 (magnified to 150 and 1200 diameters respectively). The tungsten metal is immediately surrounded by a seam of a white, hard constituent, this also forming irregular areas in the intermediate zone B, the matrix of which is ferrite (dark). This white constituent is probably an *iron tungstide*. From photo No. 49, showing the same surface after etching in boiling sodium picrate, is seen, that the tungstide is colored (brown). The tungsten metal, however, remains white, although being attacked by this reagent.

FIG. 5.
A is unmelted tungsten. B and C have been molten. D is the unchanged iron.

(b) Tungsten with steel 0.90 per cent C.

Even in this specimen the tungsten metal is surrounded by a zone of a white constituent, gradually disappearing in the surrounding steel (see photo No. 50). On account of its fern-leaf formations it has, however, another appearance than the tungstide described above. It may be assumed to be either an iron tungstide with a certain content of dissolved carbon or a double carbide with low carbon content, possibly identical with Z1. Here and there in the parts bordering on the steel, eutectic formations appear (see photo No. 51) similar to the double carbide eutectic found in the following specimen.

(c) Tungsten with steel 1.79 per cent C.

After welding, the specimen was heated to 1150° C. and quenched. This specimen contains a series of different structures gradually passing into each other (see photos Nos. 52–58). All photos are taken after heat tinting.

Close to the tungsten metal is a seam of *Z carbide* distinguished from tungsten by etching in sodium picrate. The Z carbide seam contains separate angular grains of *X carbide* (photo No. 52). From this seam branches of Z carbide forming rib-shaped eutectic congregations project (photos Nos. 52 and 53).

In approaching the steel end of the specimen eutectic austenite-Z carbide is found first (photo No. 54), then the same

eutectic associated with eutectic austenite-*cementite* (photo No. 55), which might be considered as ternary eutectic austenite-Z carbide-cementite. As seen from photo No. 55 cementite is faster heat tinted than Z carbide. Photo No. 56 shows cementite eutectic (ledeburite), two large X carbide grains and a number of small angular Z carbide grains. Photo No. 57 shows X carbide and cementite, photo No. 58 cementite only, forming ledeburite of a structure well-known from hypo-eutectic cast iron.

It should be noted that X carbide is absent in an intermediate zone, but appears close to the tungsten metal as well as at the steel end of the molten part of the specimen.

In comparing the ledeburite with the Z carbide eutectic, a distinct difference is found as to the quantity of carbide included in each of them: cementite forms the greater, Z carbide the smaller part of the mass, the balance in each case being austenite. From this as well as from its rib-shaped appearance the Z carbide eutectic is easily distinguished from ledeburite. By later experiments it was proved that the Z carbide as described here is Z_2 carbide, not Z_1 carbide.

(d) Tungsten with cast iron C = 3.1 per cent.

Fig. 6 is a longitudinal section of the specimen.

B is a rather homogeneous field, consisting of binary eutectic *austenitic-Z_2 carbide*, with primary crystals of *Z_2 carbide* (see photo No. 59). Z_2-carbide also forms a seam close to the tungsten metal. The Z_2-carbide crystals are very well defined. Twin crystals as well as crystal skeletons are seen (photos Nos. 60 to 62).

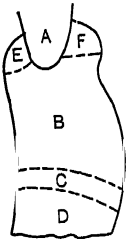


FIG. 6. A is tungsten. D is the unchanged cast iron. B, C, E and F have been molten.

D has a structure normal for white cast iron: pearlite grains dendritically arranged and ledeburite. In field C the cast iron has been fused and has dissolved tungsten. The result is that the structure of C is finer, otherwise the same as that of D. The cementite of C is more resistant to heat tinting than that of D, indicating that the former contains dissolved tungsten.

At the junction between C and D a zone of exceedingly fine

structure is found, possibly consisting of the ternary eutectic austenite Z carbide-cementite.

E and F are two fields with a structure different from that of B. As seen from photo No. 63, primary crystals of a white constituent appear in a very fine eutectic. These crystals have fern-leaf contours just as found in the welded specimen tungsten with steel 0.90 per cent C (compare photo No. 50). In the bordering zones toward B intermediate structures are found (photo No. 64).

The formation of the fields E and F is probably due to decarbonization at the surface during the welding process. The primary crystals found in E and F are probably either a tungstide or a double carbide of low carbon content, Z_1, while the double carbide of B is Z_2.

No X carbide is found in this specimen.

(e) Tungsten with cast iron C = 4.1 per cent.

The original structure of this cast iron is ledeburite eutectic. The tungsten metal is surrounded by a seam of Z carbide or some other similar constituent. Next to this seam is found *cementite*, together with *Z_2 carbide* and austenite forming a ternary eutectic. Some isolated large grains of *X carbide* are found close to the tungsten metal. The structure is seen in photo No. 65.

(f) Tungsten with cast iron 4.6 per cent.

The original structure of this cast iron is pronounced hypereutectic with large primary cementite needles in coarse ledeburite as shown by photo No. 66 in the lower right-hand corner.

The molten part of the specimen shows a similar structure, but much finer, as shown in the upper part of the same photo. In comparing the original cementite and the new, the latter is found to be more resistant to heat tinting. This is most clearly seen where the new cementite, during the solidification, has separated around the remainder of a partly dissolved cementite needle adjoining this (see photos Nos. 66 and 67). There seems to be no reason for considering the new cementite as another phase, for instance as some kind of double carbide, since it forms the same structure as the old one: primary needles in ledeburite.

On the contrary from the structure described it may be concluded that *tungsten is soluble in cementite up to a certain maximum content* without changing the cementite into another phase. As will be seen later, this fact is of a great importance for the conception of the iron-tungsten-carbon equilibrium diagram.

The structure in the vicinity of the tungsten metal is similar to that of the previous specimen with respect to the presence of a seam around the tungsten, *Z carbide* and *X carbide*. This is shown by photo No. 68.

(g) Tungsten with carbon.

The carbon specimen used for this experiment was an electrode of an arc lamp.

The welding operation caused a carburization of the tungsten metal. In preparing the specimen for microscopical examination, it was found to be very hard.

When examined before etching, the tungsten metal seems homogeneous, but its surface shows numerous scratches. It is surrounded by a continuous seam of a bright, white constituent without any scratches.

After etching in boiling sodium picrate the following was found. The tungsten metal is attacked by the reagent, thus causing the scratches to disappear. In the vicinity of the seam separations of the seam constituent are found in the boundaries of the tungsten grains, these now being visible. The surrounding seam, which appeared homogeneous before etching, is now divided in bright white grains of different crystal directions, containing separated needles of tungsten in Widmannstätten arrangement. The white constituent is probably W_3C (Ruff and Wunsch).

The mass outside the seam was very porous, probably on account of grains being loosened in grinding the specimen.

Still further away the mass was found to be solid again. The structure of this part consisted of a fine eutectic of W_3C and *X carbide*, this forming angular grains, gray-white in color and of a hardness exceeding that of W_3C (see photo No. 69).

Heat tinting attacks firstly tungsten, then W_3C and finally X carbide.

From the investigation of this specimen the conclusion can be drawn that the X carbide, found at first in the tungsten steels examined, is a *single carbide* of tungsten. Its formula (WC) was found later (see p. 60).

The hardness of the X carbide was determined by scratching tests, made with this specimen on topaz, corundum (sapphire), and diamond. Since sapphire was scratched without difficulty, its hardness lies between corundum and diamond, consequently above 9 in Mohs' hardness scale.

(4) IRON-TUNGSTEN-CARBON ALLOYS

The compositions of the alloys investigated in the following are given in Table VII below:

TABLE VII

Mark.	C Per Cent.	W Per Cent.
Wn7	1.42	3.8
C	1 00	4.6
D	2.45	4.6
Wn3	0.50	5.2
Wn6	1 73	5.5
O	1.77	17.5
N	2.70	17.4
K	0.30	28.3
M	1.80	28.4
L	2.65	27 2
H	2.73	28.0
P	3.68	47.0

These products had the following origin: Wn7, Wn3, Wn6, and K were commercial products, supplied by steel works.

The other alloys were produced as laboratory melts of about 50 g. weight in a Hanemann furnace. The ingredients used were the following:

Soft iron, C = 0.04 per cent;

B5 C = 1.29 per cent, W = 4.8 per cent;
K C = 0.30 per cent, W = 28.3 per cent;
Ferro-tungsten W = 81.5 per cent.

Carbon (sugar carbon or petroleum coke).

The results of the investigation will be given in about the same order as they were obtained.

Alloy C. C = 1.00 per cent. W = 4.6 per cent.

This alloy was obtained by remelting steel B_5 without any addition. The carbon content thus dropped through oxidation from 1.29 to 1.00 per cent.

It consisted of austenite and eutectic formations of austenite and *Z2 carbide*. The structure was very similar to that of photo No. 54. No X carbide was found, although this was the only free carbide present in steel B_5.

Alloy D. C = 2.45 per cent. W = 4.6 per cent.

The structure consisted of austenite and ledeburite. Consequently the only carbide present was *cementite*.

Pieces of this melt were subjected to annealing experiments with the following results:

After two hours' soaking at 1000° C. the eutectic congregations showed a tendency to agglomerate into solid areas of cementite; no other change was found.

After twenty-three hours' soaking at 1050° C., in a stream of nitrogen, unintentionally discontinued for some time near the end of the experiment, the following structures were found.

The interior of the specimen is illustrated by photos Nos. 70 and 71 (magnified to 100 and 1200 diameters respectively). All the cementite has disappeared and is replaced by *X carbide* in its distribution, indicating the arrangement of the previous cementite masses.

On approaching the decarbonized surface of the specimen a structure was found as shown by photo No. 72 after heat tinting. Here X carbide grains appear, surrounded by *Z carbide* areas of irregular shape, probably Z_1.

At the surface the only carbide present was Z_1 carbide.

From the structure of D after soaking, compared with those of B_5, C, and D, the following conclusions may be made.

At 4.6–4.8 per cent W.

Cementite is probably stable at 2.45 per cent C.;

X carbide is undoubtedly stable at some lower range of carbon contents; Z_1 carbide is probably stable at still lower carbon contents.

Alloy K, C = 0.30 per cent; W = 28.3 per cent.

This alloy was in the form of an ingot 3 inches square.

It contained two constituents about half of each. One of them was hard and formed white, rounded grains with tattered contours, the other being soft and resembling ferrite.

After hardening from different temperatures from 700 to 1200° C. no change in structure was found.

The hard constituent ought to be the same as that found in the welded specimen tungsten with soft iron, assumed to be an *iron tungstide*, and probably contains some dissolved carbon.

Alloy Wn3. C = 0.50 per cent. W = 5.2 per cent.

The steel was in the form of a forged bar 18 by 10 mm.

It contains very small quantities of *Z carbide* in small round grains, probably Z1 carbide.

Alloy Wn6. C = 1.73 per cent. W = 5.5 per cent.

The steel was forged into a 27-mm. round bar.

It showed a dull surface after polishing.

A specimen hardened from 800° C. contained large quantities of *cementite* and *X carbide*, but no Z carbide.

Another specimen hardened from 1200° C. showed only *X carbide*. The cementite was dissolved.

On cooling to 750° C. cementite separated again.

Alloy Wn7. C = 1.42 per cent. W = 3.8 per cent.

The steel was forged into a 2-in. square bar.

The polished surface was dull.

In a specimen, hardened from 800° C., three carbides were present: *X carbide*, *Z carbide*, and *cementite*, indicating lack of equilibrium.

Another specimen, hardened from 1200° C., contained only one carbide: *X carbide.*

A third specimen was heated to 1200° C., and then cooled to 750° C. and hardened. It contained *X carbide* and *cementite*, the latter as needles and seams in the austenite grain boundaries. *No Z carbide was present.*

Consequently, Z carbide is unstable at this composition and, therefore, decompposes on proper heat treatment. The presence of Z carbide in the original structure can be attributed to the large dimensions of the steel: it had undoubtedly been subjected

to a lesser degree of heat treatment and hot working than, for instance, steel Wn6.

Alloy H. C = 2.73 per cent. W = 28.0 per cent.

The crucible with the molten alloy was removed from the furnace and allowed to cool in the air. As soon as the melt had solidified, it was quenched in water.

In the structure the following constituents are found: *austenite*, *Z2 carbide*, *cementite*, and *X carbide*, in the following combinations:

Binary eutectic *austenite-Z2 carbide* appears in numerous fields with contours duplicating the directions of the structure inside these fields, thus indicating that these masses have solidified before the masses between. (See photos Nos. 73, 74, and 75.) This eutectic has the rib-shaped appearance described before, often contains *primary crystals of Z2 carbide* of a well-defined symmetric shape.

These are usually hollow, in their turn containing eutectic (see photos Nos. 73 and 75). It is obvious that in this eutectic Z2 carbide is crystallographically leading, while austenite is dominating in regard to quantity. In each eutectic system the carbide veins follow the same directions.

It might reasonably be expected that the balance of the mass would consist of a ternary eutectic, containing austenite, Z2 carbide, and a third constituent. The main constituent in these areas is, however, cementite in the form of long and wide needles with a primary appearance. The narrow spaces between these are occupied partly by austenite, Z2 carbide and cementite in fine distribution, partly only Z2 carbide and cementite, and partly only austenite in dendritic (apparently primary) arrangement.

Obviously this mass, being the last part solidified, can only *partially* be considered as *ternary eutectic austenite-Z2 carbide-cementite*. A pronounced feature is that cementite is the constituent dominating in quantity and generally also crystallographically, the exception being Z2 carbide.

In the heterogeneous structure isolated *X carbide* grains appear, about 0.2 mm. maximum. Most of them are apparently formed by decomposition of Z2 carbide and some are also found in cementite.

The bottom part of the melt has an appearance different from the one described above, as will be seen from photo No. 76.

The Z_2 carbide grains are not so large and are solid and angular in shape. They are mostly surrounded by austenite areas in about the same quantity. The rest seems to be ternary eutectic austenite-Z_2 carbide-cementite.

Another part of the melt H was quenched from the molten state by casting it in a thin mold of silver plate standing in water and was consequently very rapidly cooled.

The structure of this melt is similar to the structure first described of alloy H, the grains only being finer. Furthermore *X carbide is absent.*

Alloy L. C = 2.65 per cent. W = 27.2 per cent.

This melt, having approximately the same composition as the former one, was allowed to cool slowly in the furnace, until it had solidified and was then quenched.

It contains the following fields of different structures: *binary austenite-Z2 carbide eutectic*, with a slight amount of *primary Z2 carbide crystals, ternary austenite-Z2 carbide-cementite* eutectic. *X carbide* in great quantities, mostly at the surface.

Part of the X carbide grains were apparently separated as primary crystals from the molten alloy, since they have a well-defined crystal shape, to which the adjoining austenite-Z_2 carbide eutectic has accommodated itself. Another part of the X carbide grains are formed by partial or complete decomposition of primary Z carbide crystals. Furthermore, rib-shaped pseudo-eutectics austenite-X carbide are found, formed by decomposition of austenite-Z_2 carbide eutectics.

Alloy M. C = 1.80 per cent. W = 28.4 per cent.

The greater part of this melt has a structure similar to the previous one.

In the upper part a different structure has developed, consisting of large *dendritic austenite grains*, consequently primary, partly in a *ternary eutectic austenite-Z2 carbide-cementite*, and partly in a *ternary eutectic austenite-T-cementite*, T being a kidney shaped constituent, situated between Z_2 carbide and cementite in heat tinting qualities. Large cementite needles are also found embedded in this ternary eutectic. No X carbide is found.

Alloy N. C = 2.70 per cent. W = 17.4 per cent.

Through the whole melt are found a great many primary *austenite dendrites*, surrounded by large cementite needles, the matrix between these structure formations consisting mostly of *austenite-T-cementite*. Possibly, austenite and cementite together constitute a binary eutectic.

Furthermore are found:

Isolated *austenite-Z2 carbide eutectics* in small congregations, adjoining the austenite grains and

X carbide grains, formed from Z2 carbide.

Apparently the existence of two different binary eutectics is due to undercooling. One of them is less stable than the other.

Alloy O. C = 1.77 per cent. W = 17.5 per cent.

The greater part of the surface is occupied by *austenite dendrites*.

The remainder consists of *binary eutectic austenite-T* in the upper and inner portion, *binary eutectic austenite-Z2 carbide* in the lower and outer portion.

Alloy P. C = 3.68 per cent. W = 47.0 per cent.

This alloy was produced for the purpose of getting a material, from which X carbide in great quantity could be separated and then analyzed.

In the structure are found the following constituents: *primary X carbide crystals*; *primary Z2 carbide crystals*, partly transformed into X carbide; small rounded *X carbide grains* in swarms together with austenite (binary eutectic) surrounding the primary X carbide crystals; *binary austenite-Z2 carbide eutectic*; a matrix, containing *austenite*, *cementite*, and probably *T*.

This product was subjected to a number of annealing experiments at 1000° C., each for a period of seven hours, with subsequent quenching. On examination in the microscope, the X carbide was found gradually to increase at the cost of Z2 carbide and cementite. After ten heat treatments there remained, besides carbide and austenite, a slight quantity of a third constituent, either T or cementite. This heat-treated product, finally hardened at 1000° C. to dissolve the excessive cementite,

was dissolved in dilute acid in order to separate the X carbide (see part B6 to follow):

The results of this part of the investigation will be summed up in part B7. It may, however, be stated here, as a general impression, that in many of these iron-tungsten-carbon alloys constitutional equilibrium was not reached on account of undercooling taking place in solidifying. This is evident not only from the number of constituents present in the same alloy, which, in the case of equilibrium, should not exceed 3, but also from the many different combinations of the constituents found in the same specimen.

(5) PARTIAL MELTING OF TUNGSTEN STEELS

When a steel is rolled or forged, any carbide eutectic present is broken up into separate grains, the eutectic structure thus being destroyed. This structure, however, is one of the characteristics, from which a certain carbide may be distinguished from others, and, in tungsten steels a very valuable characteristic, since in this system different carbides with similar etching qualities seem to occur. It was therefore considered that remelting of the commercial steels, included in this investigation, would give good information in this respect. Since heating just into the melting range is sufficient for producing the carbide eutectic in question on subsequent cooling, experiments with *partial* melting were carried out on steels containing a considerable amount of carbide.

A small specimen was heated in the open air by means of an acetylene-oxygen flame, until it began to melt, this moment being observed by the eye. The heating was then discontinued and the specimen allowed to cool in the air to about 1100° C., and then quenched. It is assumed that no decarbonization of the main part of the specimen took place on account of the short time of heating, which was less than one-half minute.

The results will be seen from Table VIII.

TABLE VIII

Steel Marked.	C Per Cent	W Per Cent.	Carbide.	
			Before Melting.	After Melting.
Wn3	0.50	5 2	Z_1 (?)	Z_1
6	0.61	6.4	Z_1 (?)	Z_1 and Z_2
B5	1.29	4.8	X	Z_2
Wn7	1.42	3.8	X and Z_2 (?)	Z_2 in small, cementite (?) in large quantity, and T (?)
Wn6	1.73	5.5	X	

The eutectics Z_1 and Z_2 were very different, the latter being rib-shaped, the former having a knotty appearance with the carbide occupying the greater part of its mass.

The results may be summed up as follows:

At a temperature just below solidifying; Z_1 is the only stable carbide of steels Wn3 and 6; X is the only stable carbide of steels B5, Wn7, and Wn6.

Undercooling occurred in the remelted steels B5, Wn7, and Wn6, and probably in 6. For that reason X carbide, having a slow crystallization rate, did not reappear after melting in any of the steels, in which it was found before melting. Instead were found: in steel B5: the unstable Z_2 carbide; in steels Wn7 and Wn6 three unstable carbides, Z_2, cementite (?) and T (?).

(6) SEPARATION AND ANALYZING OF THE X CARBIDE

For this purpose a product was produced, containing X carbide as the only carbide visible in the microscope.

This product was crushed and dissolved in dilute sulphuric acid, 1 per cent solution being used in the preliminary, and 5 per cent in the final experiments. The dissolving was hastened by heating to about 60° C. The clear solution was at intervals removed by decanting and fresh dilute acid added. The moment of complete dissolving was determined by magnet on the dried residue. The residue was then washed repeatedly with distilled water, and alcohol and then dried at 100° C.

If the dried residue contained tungstic acid, this was removed by 1 per cent sodium hydroxide solution and the residue washed again.

In analyzing, *carbon* was first determined by combustion in oxygen and absorption of the carbon dioxide in potassium hydroxide.

The oxide formed was then fused with potassium sodium carbonate, leached in water and filtered. The precipitate was burned and weighed as ferric oxide, from which *iron* was calculated. The ferric oxide was dissolved and the solution titrated, to obtain a control of the iron content.

The filtrate was diluted to 500 cc. and 100 cc. of it precipitated with hydrochloric acid. The precipitate was burned and weighed as tungstic acid, from which the *tungsten* content was calculated.

Dissolving experiments, as described above, were made on steel B5 and alloy P.

Steel B5.

The specimens subjected to dissolving were hardened at 1000° C. On examination in the microscope no other carbide than X carbide was detected.

Two experiments were made with results as follows:

Weight of Sample, Grs.	Weight of Residue, Grs.	Composition of Residue.			
		C Per Cent.	Fe Per Cent.	W Per Cent.	Total Per Cent.
38.277	1.2082	7.14	1.60	86.17	94.91
33.863	0 9618	7.07	2 40	85 81	95.28

The residue has a dark-gray color and was nonmagnetic.

The total percentages arrived at in these determinations are unsatisfactory. Therefore special determinations of Cr, Mo and Va were made on the steel. None of these elements, however, were present.

In decanting and washing the residue a light powder was noticed floating in the liquid above the sediment. Therefore the carbide was probably mixed with carbon, formed by decomposition (compare Arnold and Read), possibly from cementite, notwithstanding no cementite was found by microscopic examination of the hardened steel.

These experiments, although their results are inconsistent as to the composition of the carbide, give, however, an approximate idea of the quantity of the X carbide present in this steel. The average carbide content was found to be about 3 per cent. This figure was used as a basis for calculation of the composition of the austenite in steel B5.

Alloy P.

In the manner described above a part of this alloy was annealed for seventy hours at 1000° C., and finally quenched at that temperature. The structure then consisted of martensite and X carbide, only traces of another carbide being visible in the microscope.

Two dissolving experiments were made. The results were as follows:

Determination.	C Per Cent.	Composition of Residue.		
		Fe Per Cent.	W Per Cent.	Total Per Cent.
1	6.21	1.03	92.65	99.89
2	6.27	1.07	92.38	99 72

Since the composition of WC is 6.12 per cent C and 93.88 per cent W, it can be considered as proved that *X carbide constitutes mono tungsten carbide WC*, possibly with a low content of dissolved iron. This carbide as previously stated is a nonmagnetic dark-gray powder of a hardness between corundum and diamond.

(7) REVIEW OF CARBIDES AND SIMILAR CONSTITUENTS FOUND IN MICROSCOPIC INVESTIGATION OF IRON-TUNGSTEN-CARBON ALLOYS

Fe_nW, Iron Tungstide.

A white, hard constituent forming grains of shattered contours. The tungstide is colored brown by boiling sodium picrate and is rather resistant to heat tinting. It was found in alloy K (C = 0.30 per cent, W = 28.3 per cent) and in the welded specimen tungsten with soft iron (C = 0.04 per cent). It might be identi-

cal with Fe_3W, assumed by Swinden, or Fe_2W, suggested by Arnold and Read. It is stable in iron-tungsten-carbon alloys with low carbon content and a tungsten content sufficiently high for its appearance.

Z1 Carbide. A white, hard constituent, forming rounded grains. It is colored by boiling sodium picrate and is rather resistant to heat tinting. It was found in the steels Wn3 (C = 0.50 per cent, W = 5.2 per cent) and 6 (C = 0.61 per cent, W = 6.4 per cent). In the remelted steel 6 it formed eutectic of a knotty appearance. It is probably the same constituent as was found in the welded specimens tungsten with steel (C = 0.90 per cent) and tungsten with cast iron (C = 3.1 per cent), decarbonized portion, forming fern-leaf-shaped primary crystals and a fine eutectic with austenite. Its formula may be Fe_2W_2C (Arnold and Read; see later discussion). It is probably stable at medium carbon content.

Z2 Carbide. A white, hard constituent. It is colored by boiling sodium picrate and eaten out on prolonged action. It is rather resistant to heat tinting. It forms primary crystals of a well-defined shape, sometimes appearing as twin crystals. Its binary eutectic with austenite has a characteristic rib-shaped appearance, dominated crystallographically by the carbide, while the austenite occupies the greater part of its surface. It was always found crystallized from the molten phase, never separated from austenite in the solid state as in the case of cementite. It was found in the partially melted steels 6 (C = 0.61 per cent, W = 6.4 per cent), B5 (C = 1.29 per cent, W = 4.8 per cent), Wn7 (C = 1.42 per cent, W = 3.8 per cent) and Wn6 (C = 1.73 per cent, W = 5.5 per cent), in all melts, except C (C = 2.45 per cent, W = 4.6 per cent) and in the welded specimens tungsten with steel (C = 1.79 per cent) and tungsten with cast irons (C = 3.1, 4.1 and 4.6 per cent). It contains more carbon than Z1 (compare carburization experiments with 6). It is easily decomposed into WC and austenite at a high temperature. It is consequently a metastable double carbide.

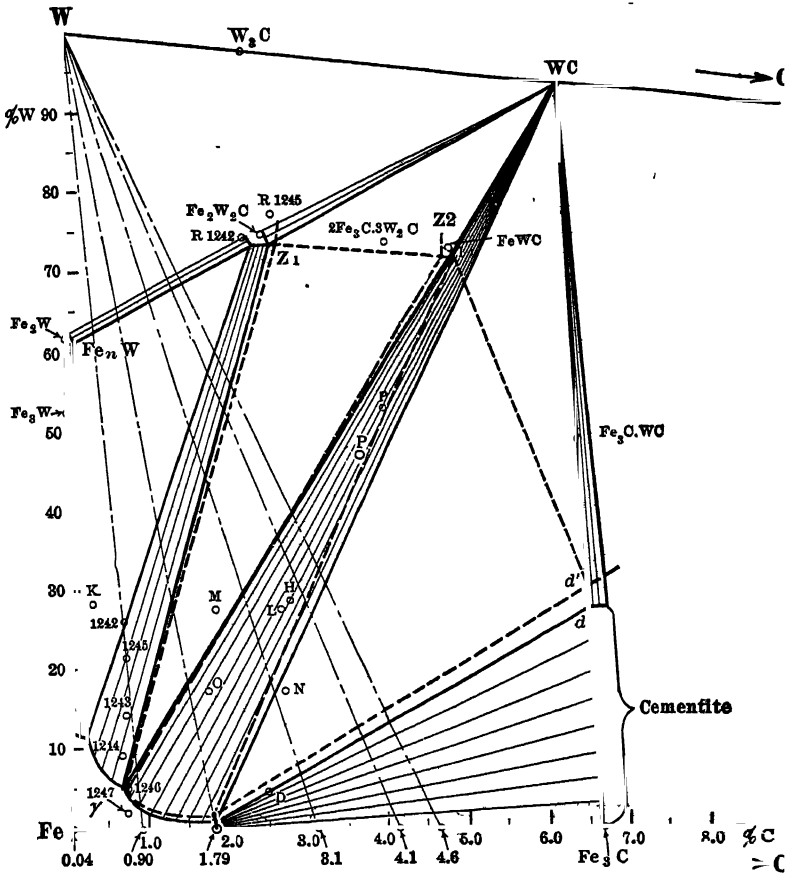
T. A white, hard constituent, colored by boiling sodium picrate. It responds to heat tinting faster than Z2 but more slowly than cementite. It was noticed in the partially melted

steels Wn7 and Wn6 and in the melts M, N, O and P. It is probably a metastable double carbide.

Cementite. A white, hard constituent, which is colored by boiling sodium picrate and shows less resistance to heat tinting than other carbides, found in iron-tungsten-carbon alloys, but greater resistance than cementite Fe_3C in iron-carbon alloys When crystallizing from the molten alloy, it forms large needle-shaped primary crystals as well as ledeburite eutectic just like cementite Fe_3C in iron-carbon alloys. It is, furthermore, separated from solid solution in hyper-eutectoid austenite and forms pearlite as does cementite Fe_3C in iron-carbon alloys. When crystallizing from the molten state in welding tungsten with cast iron, it was found to form continuous envelopes around the pre-existent tungsten-free Fe_3C crystals of the same structure as these, only differing in regard to heat-tinting qualities. When alloy D (C = 2.45 per cent, W = 4.6 per cent), containing only this carbide and austenite, was heated for a long time at 1050° C., exposed to some oxidation, it was found to decompose into WC and austenite. These evidences point to the fact that this carbide constitutes the same phase as cementite Fe_3C, with which it forms a continuous range of solid solution with the tungsten content varying as the total composition of the alloy varies.

It seems not unlikely that the tungsten amount dissolved in cementite is accompanied by an equivalent amount of carbon, i.e., that WC molecules are dissolved in the cementite, since WC was found to be a decomposition product of cementite. Theoretically, it ought to follow that the cementite reaches its maximum tungsten content (d' in Plate 1) when in equilibrium with Z2 carbide, and since Z2 is metastable, this cementite should also have a metastable composition and consequently be subject to decomposition, separating WC and reducing its tungsten to a point (d in Plate 1), which is the maximum tungsten content of the stable cementite. In accordance herewith, WC was found as a decomposition product of cementite in the alloys H and P. Since Fe_3C is metastable, the stable phase being graphite, it may be assumed that at a low tungsten content the cementite is unstable and liable to form graphite. Consequently,

PLATE 1.



Tentative Equilibrium Diagram Fe-W-C.

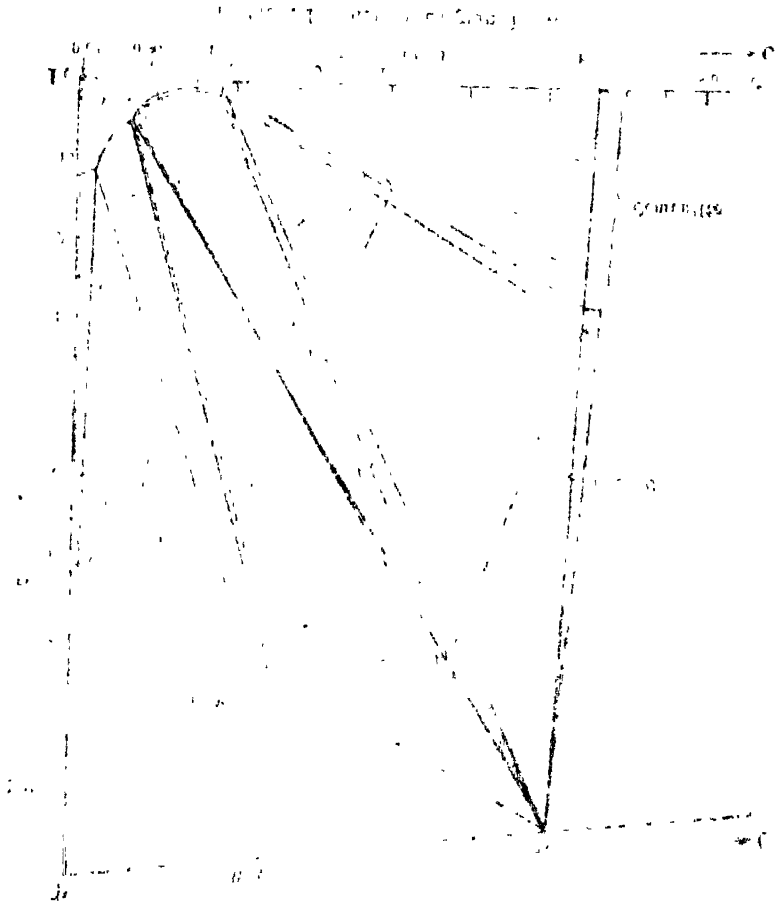
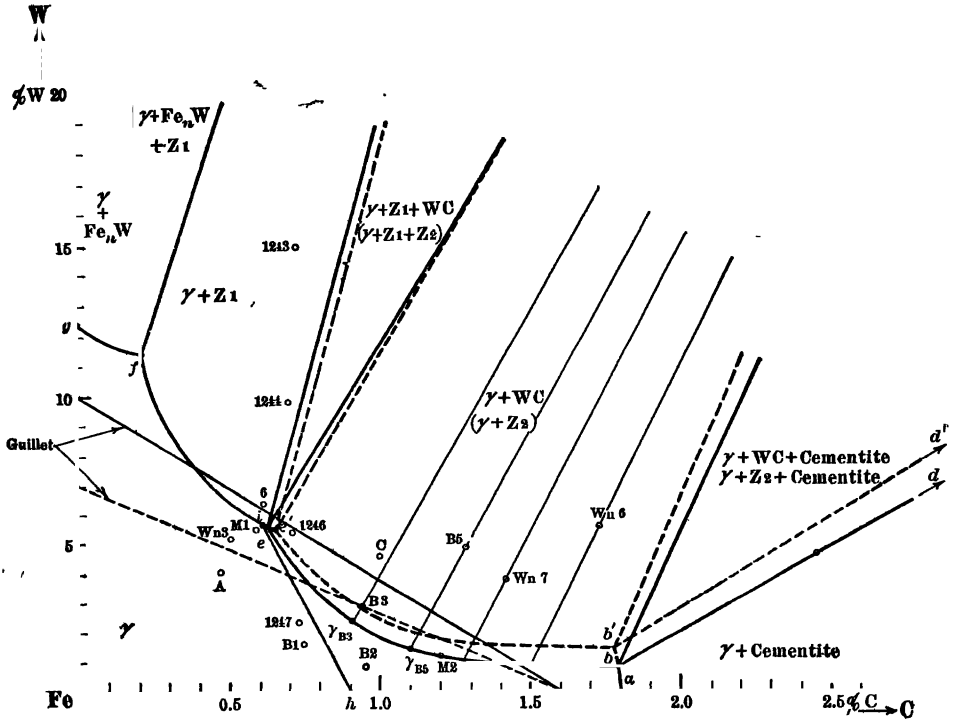


PLATE 2.



Tentative Equilibrium Diagram Fe–W-C.

the stable range of cementite is surrounded by one metastable range at low tungsten content, and another at high.

Cementite was found in alloy D, as the only carbide present; in all melts, forming ledeburite with or without primary crystals; in all hyper-eutectoid tungsten steels, separated from austenite, and in all tungsten steels as a constituent in pearlite.

WC, gray-white constituent, harder than corundum. It is not colored by sodium picrate. It has the greatest resistance to heat tinting of all constituents examined. Under favorable conditions regular crystals are formed with angular shape. It was found as primary crystals, separated from the molten alloy, and as a decomposition product, formed in the solid alloy at high temperatures from Z2 or cementite (probably also from austenite), when sufficient time had been allowed. It is a stable carbide. It was found in the steel B2, B3, B5, Wn6, and Wn7, in the melts H, L, N, and P, and in the welded specimens tungsten with steel (C = 1.79 per cent) tungsten with cast irons (C = 4.1 per cent and 4.6 per cent) and tungsten with carbon.

W_3C (probably), a white, hard constituent. It is not colored or attacked by boiling sodium picrate, and is more resistant to heat tinting than tungsten but less than WC. It was found only in the welded specimen tungsten with carbon, and not in iron-tungsten-carbon alloys.

C. TENTATIVE IRON-TUNGSTEN-CARBON DIAGRAM

The results obtained, however incomplete they are in regard to the compositions and reciprocal solubility of the phases, will be utilized for constructing a tentative equilibrium diagram. Certain parts thereof will be merely schematic.

The most used type of a ternary diagram equilateral triangle, is unsuitable in this case, giving too indistinct representations. Instead rectangular coordinates will be employed with the scale of carbon content ten times that of tungsten. The whole diagram thus assumes the form of a rectangular triangle, one side being ten times as long as the other. This type, incidentally, could preferably be used for all ternary steels.

In Plate 1 a partial Fe-W-C diagram is drawn. Plate 2 gives

the same on a larger scale, mostly for illustration of the shape and dimensions of the austenite field.

The diagram refers to a temperature just below solidification.

As is seen, the austenite, i.e., the γ-iron with a varying content of dissolved carbon and tungsten, is limited in different directions by the four curves *a–b*, *b–e*, *e–f*, and *f–g*; *a–b* indicates the composition of austenite in equilibrium with cementite,[1] *b–e* with WC, *e–f* with Z1 and *f–g* with Fe_nW.

In the metastable Z2 system the curve *b–e* is substituted by *b'e'*, which indicates the composition of austenite in equilibrium with Z2.

The remainder of the diagram given is divided in the following fields:

a–*b*–*d*–Fe_3C : austenite+cementite.
b–WC–D : austenite+cementite+WC.
b–*e*–WC : austenite+WC.
e–Z1–WC : austenite+WC+Z1.
e–*f*–Z1 : austenite+Z1.
f–Fe_nW–Z1 : austenite+Z1+Fe_nW.
f–*g*–Fe_nW : austenite+Fe_nW.

The metastable (Z2–) system is divided as follows:

a–*b'*–*d'*–Fe_3C : austenite+cementite.
b'–Z2–*d'* : austenite+cementite+Z2.
b'–*e'*–Z2 : austenite+Z2.
e'–Z1–Z2 : austenite+Z1+Z2.
e'–*f*–Z1 : austenite+Z1, etc.

Since Z2 is metastable and WC stable, the austenite contains more tungsten and carbon when in equilibrium with Z2 than with WC.

The locations of the points *b*, *d*, *e*, *f*, *g*, Z1, Z2, *b'*, *d'*, and *e'* are not established. On the basis of the microscopic investigations as well as other available data certain parts of the diagram may be drawn approximately, as follows:

The point *a* (Plate 2) is about 1.8 per cent C according to previous investigations. The direction of *a–b* is not known. As to the curve *b–e* the following data were found. The steels B3, B5, Wn7, and Wn6 contain WC in different quantities. Con-

[1] The stable system austenite-graphite is not considered here.

sequently *b–e* must run below the points B3, B5, Wn7, and Wn6 in the diagram and intersect the extended lines WC–B3, WC–B5, etc., at distances from B3, B5, etc., proportional to the WC content. These intersection points are called γ_{B3}, γ_{B5}, etc. and represent the compositions of the austenite phases of these steels.

In this connection an investigation by Mars [1] may be referred to. He gives data on residual magnetism Br obtained on hardened tungsten steels with different carbon and tungsten contents. The steels were divided in two series, one of them with C = 0.57–0.61 per cent, the other with C = 1.15–1.25 per cent. In the former series Br increased with the tungsten content, reaching a maximum at 5.5 per cent; higher tungsten contents than 5.5 per cent were not examined. In the latter an increase in Br was found up to 1.2 per cent W and with higher tungsten content there was a decided drop in Br. This was probably due to the fact that at 0.59 per cent carbon the maximum tungsten content dissolved in austenite is about 5.5 per cent and at 1.20 per cent carbon it is about 1.20 per cent tungsten. These two compositions will be called M_1 (C = 0.59 per cent, W = 5.5 per cent) and M_2 (C = 1.20 per cent, W = 1.20 per cent). Consequently, the point M_2 should be on the curve *b–e* (this implies the assumption, that the steel, examined by Mars, belonged to the stable system austentite—WC). This conclusion was therefore applied in drawing the curve *b–e* in the present diagram.

As the curve *b–e* is drawn, γ_{B5} is at C = 1.10 per cent, W = 1.5 per cent, which means abandoning the approximate figure previously calculated, C = 1.14 per cent, W = 2.0 per cent. This correction seems justified, since the calculation was based upon a determination of the carbide content, which admittedly may be somewhat inaccurate. B3 is located at the composition, previously estimated: C = 0.91 per cent, W = 2.4 per cent. As to steel B2 (C = 0.95 per cent, W = 0.95 per cent) a contradiction exists, since it actually contains traces of WC, and consequently *b–e* should run a trifle below B2. A consequence hereof would be,

[1] G. Mars: "Magnetstahl und permanenter Magnetismus," Stahl und Eisen, 1909, Nos. 43 and 45. (See also E. Heyn: Handbuch der Materialienkunde, II, 1912.)

that γ_{B3} would contain less tungsten than γ_{B1}, which, however, conflicts with the fact, that B5 and B1 showed about the same degree of stabilization after heating to a high temperature. For that reason *b–e* has been drawn above B2, the assumption being that the presence of WC in this steel is due to heterogeneity of composition, caused by selective freezing. Since no carbide was found in steel B1, *b–e* is drawn above the point B1.

The point *e* is assumed to be at 0.6–0.7 per cent C, 5–6 per cent W. This is supported by the fact that steel 6 contained Z1. The curve *e–f* is drawn above Wn3, the carbide content of which was small and explained by selective freezing. The point M1, inferred from Mars' investigation, is located in the vicinity of *e–f* in accordance with the discussion just presented.

The curves *e–f* and *f–g* are only tentative.

Above the curve *b–e* is drawn *b'–e'*, representing the composition of austenite when in equilibrium with Z2.

The linc *h–i* represents the eutectoid compositions of the austenite at different tungsten contents and is tentatively drawn according to the results obtained in Section I.

As to the other phases in the iron-tungsten-carbon system, nothing is known of their solubility in each other, except that cementite dissolves tungsten. Each phase, however, is represented in the diagram by an area, assuming a certain variation of its composition. The possible compositions of Fe_nW, Z1 and Z2 will be discussed later in connection with the results obtained by other investigators. As stated before, cementite ought to have a higher tungsten content (*d'*) when in equilibrium with the metastable Z2 than with the stable WC (*d*). The alloy D contained cementite but no Z2 and showed no signs of decomposition of the cementite after annealing at 1000° C. for two hours. D is therefore below *b'–d'* and probably even below *b–d*.

It was expected, that the structure of the melts H, L, M, N, O, and P would give good information concerning certain parts of the diagram. This was not the case, however, as stated before, since all structures showed signs of undercooling and lack of equilibrium. The two- and three-phase combinations austenite-T, austenite-T-cementite, austenite-Z2 and austenite-Z2-cementite appear in these structures apparently inconsistently.

The only definite conclusions to be made from the structural examination are that austenite is primarily separated from the molten alloy in N and O, and Z_2 in P, H, and L. This gives a guidance in drawing the lines of eutectic composition, but because of the few facts available this will not be attempted.

Regarding the welding experiments, the range of compositions existing in a specimen ought to follow a line in the diagram drawn between the two members welded together. Whether these lines are straight as drawn in Plate 1 or not, depend on the diffusion conditions existing and the procedure in welding. These reservations made, the following data may be inferred from the structures of the welded specimens.

The line W—soft iron 0.04C passes a structure field containing Fe_nW.

The line W—steel 0.90C passes a structure field containing Z_1.

The line W—steel 1.79C passes the hypo-eutectic austenite-Z_2 range.

The line W—cast iron 3.1 passes the hyper-eutectic austenite-Z_2 range.

The line W—cast iron 4.1C possibly passes the ternary eutectic austenite-Z_2-cementite.

The line W—cast iron 4.6C possibly passes the ternary eutectic austenite-Z_2-cementite.

WC was found in the welded specimens W with 1.79C, W with 4.1C and W with 4.6C but not in W with 3.1C, this apparently due to undercooling.

The specimen W with C contained W_3C (?) and WC.

These results from the welding experiments agree with the diagram drawn.

D. CRITICISM OF PREVIOUS INVESTIGATIONS

Two pure tungsten carbides were observed in the author's investigation; one of them, *WC*, was found in the W–C as well as in the Fe–W–C system; the other, probably W_3C, only found in the W–C system. These results agree with those of Ruff and Wunsch and in regard to WC with those of Williams.

No evidence was found for the existence of W_2C, stated by Moissan and supposed by Ruff and Wunsch. Possibly, the

product found by Moissan was a mixture of W_3C and WC, for instance their eutectic observed by the author in the welded specimen tungsten with carbon.

Arnold and Read stated the presence of WC in alloys with about 0.7 per cent carbon and different tungsten contents. This is probably an erroneous interpretation of the results of their experiments and will be discussed later.

Williams found a double carbide $2Fe_3C$, $3W_2C$, or $Fe_6W_6C_5$. This carbide may exist and may be the same as Z_1 or Z_2, found by the author. Its existence was, however, not proved, since the homogeneity of the product was not verified by microscope at high magnification.

As to $Fe_3C \cdot WC$, found by Carnot and Goutal in steels of 2.0–2.2 per cent C and 6.1–7.8 per cent W, it may have consisted of a mixture of cementite (with W dissolved) and WC. If it was a homogeneous product, it must constitute the same phase as cementite, the range of which should then be extended to that point in the author's diagram.

The diagram of Guillet, which is included in Plate 2, shows the distribution of double carbide in the iron-tungsten-carbon system. It agrees roughly with the author's tentative diagram in regard to the extension of the austenite phase. The assumption, that only one carbide exists does not, obviously, cover the facts. Guillet's observation, that the carbide grains had less distinct contours at higher tungsten contents is explained by the fact that in raising the tungsten content, the carbon content remaining constant, the carbide constituent may pass from one carbide to another with lower carbon content or even to Fe_3W.

Fe_3W assumed by Swinden, may be identical with Fe_3W, described by the author.

The most complete investigation made of the carbides in tungsten steels is that of Arnold and Read.

The steels examined by Arnold and Read had a carbon content of about 0.7 per cent and a tungsten content from 2.36 to 26.29 per cent as seen from Table IX. The steels are plotted in Plates 1 and 2. Samples of the steels were annealed for six hours at 950° C., with subsequent slow cooling for twelve hours to normal temperature. The annealed sample swere electrolyt-

ically dissolved in dilute hydrochloric acid. In analyzing the residue the following results were obtained (see Table IX).

TABLE IX

				Residue Obtained.				Theoretical Composition of Residue.		
Steel	C Per Cent.	W Per Cent.	Quantity, Per Cent.	C Per Cent.	W Per Cent.	Fe Per Cent.	Formula.	C Per Cent.	W Per Cent.	Fe Per Cent.
1247	0.73	2.36	6.2	14.42	33.29	52.29	$6WC+10Fe_3C+23C$	14.39	33.94	51.68
1246	0.71	5.37	8.1	8 82	62 22	28.96	$8WC+4Fe_3C+5C$	8.69	62.69	28.63
1244	0.70	9.74	10.6	6.45	89.25	4.30	$19WC+Fe_3C$	6.15	89.55	4.30
1243	0.73	14.96	11.5	5.56	88.06	6.38	$7WC+Fe_2W$	5.04	88.25	6.71
1245	0.725	21.15	21.3	2.55	77.30	20.15	$4WC+3Fe_2W$	2.87	77.03	20.10
1242	0.67	26.29	23.5	2.18	74.50	23.32	$WC+Fe_2W$	2.44	74.74	22.76

Against the method of analyzing residues of *annealed* steels, the objection may be raised that constituents possibly present in free form at high temperatures will be found in the residue mixed with the carbide component of possibly formed pearlite.

Accordingly, the residue can be homogeneous only in the following two cases:

(1) No pearlite transformation has taken place during annealing; the residue then consists of the free constituent at high temperature.

(2) No free constituent exists at high temperature; the residue then represents the carbide constituent of the pearlite.

The former may be true in steels Nos. 1245 and 1242 (see Table IX and Plate 1), due to the probably high tungsten and low carbon content of the matrix. The residue compositions of these two steels are plotted in Plate 1 as R_{1245} and R_{1242} and support the tentative assumption made by the author, that both these residues have been composed of Z_1 carbide, this carbide being $Fe_2W_2C(Fe_2W \cdot WC)$. Arnold and Read, on the other hand, believe these residues to be mixtures of Fe_2W and WC, although they could not distinguish between the two in the microscope, nor separate them chemically. They state that WC is colored by boiling sodium picrate just like Fe_2W. As far as WC is concerned, this is obviously a mistake, as has been shown by the author. On the other hand, Fe_2W may be present

in steels of high tungsten but lower carbon content: the author's Fe_nW.[1]

Alternative two was probably true in the case of steel 1247. Unfortunately, the residue of this steel was partly decomposed in dissolving the steel as seen from the high carbon content. No formula of the carbide can therefore be calculated. The author believes the carbide was homogeneous and consisted of cementite with high tungsten content.

The residue of steels 1246, 1244, and 1243 were probably heterogeneous mixtures, since free carbide would be expected in the steels (compare Plate 2). No conclusion will therefore be drawn from the composition of these residues.

Arnold and Read's conclusions (compare p. 43) that on increasing tungsten content in the steel, the cementite (Fe_3C) of the pearlite is gradually displaced by " tungsten cementite " WC, the latter forming "tungsten pearlite," rests upon the fact that an increasing percentage of tungsten was found in the residues as well as on the erroneous assumption that WC is colored by boiling sodium picrate. It seems more plausible that the increasing tungsten content of the carbide constituent of pearlite is due to an increasing amount of tungsten dissolved in cementite, possibly as WC molecules. If WC has been present in some of Arnold and Read's steels (e.g., 1246; compare Plate 2), it has probably been as a free carbide and not as a partner in pearlite.

It is suggested that the term " tungsten cementite," proposed by Arnold and Read for WC, should not be used or it should be used for cementite containing tungsten dissolved.

Arnold and Read state that no double carbide is present in tungsten steels, since in all steels investigated by them, the compositions of the residues could be approximately obtained by assuming the presence of Fe_2W, WC, and Fe_3C in different proportions. This reasoning, however, is not conclusive, since a double carbide may have a formula like $mFe_2W \cdot nWC$ or $mFe_3C \cdot nWC$. The author's microscopical observations indicate with a high degree of probability that at least one or two, probably more double carbides exist, more or less stable.

[1] Compare Appendix.

E. SOME PRACTICAL CONSEQUENCES OF FREE CARBIDES IN TUNGSTEN STEELS

The most suitable composition of tungsten steel for permanent magnets has been found to be about 0.6 per cent C and 5 to 6 per cent W. This composition may be considered as the practical limit arrived at in increasing the carbon and tungsten contents of the steel in order to obtain a maximum permanent magnetism in the hardened steel, this property being a function of the composition of the solid solution. If the tungsten content is further increased, more double carbide is formed without the composition of the austenite being materially changed (it is slightly displaced toward a lower carbon content). If the carbon content is increased double carbide also appears, or possibly WC, and the tungsten content dissolved in the austenite decreases. In this connection an experience may be mentioned made some years ago by a steel works manufacturing tungsten magnet steel. Sometimes it was found, that the magnet steel showed a noticeably lower permanent magnetism. At the same time a change in structure was observed. Numerous small points occurred, usually spread over a field of the cross-section extending from the surface to a certain depth. Probably these points were small WC grains, caused by some change in heat treatment or composition. The formation of WC implies obviously a change to the stable system, the content of carbon and tungsten in the austenite therefore being lowered with resulting decrease of magnetic qualities of the hardened steel.[1]

It follows from the investigations made that in tungsten steels with a carbon content higher than about 0.7 per cent and with sufficient tungsten content, the steel may be at will brought into the stable system austenite-WC, or the metastable austenite-double carbide (Z_2). When high contents of C and W in the austenite are wanted, apparently the latter system is preferable. One should then avoid too slow cooling after solidification, too

[1] Recently, the author had occasion to examine a magnet steel of the following composition: 0.65 per cent C, 7.1 per cent W. It contained a considerable quantity of WC grains together with Z_1 grains. Its carbon and tungsten contents were probably too high for a magnet steel.

high temperature in hot working, and too long heating before hot working or in annealing.

On the other hand, WC, on account of its great hardness, is probably a desirable constituent in cutting tools for machining hard material, for instance chilled rolls. The proper heat treatment for these steels would apparently be the reverse of the one just described.

One consequence of the form of the curve *b–e* respectively *b'–e'* in the diagram, is that the more the tungsten content is raised above this curve, the carbon content remaining constant, the more carbon is absorbed by the free carbide, either WC or Z_2. Assuming the stable system austenite-WC to be established this fact is illustrated by Table X, showing the approximate compositions, deduced from the tentative diagram, of the austenite phases of three selected tungsten steels of the same carbon content 1.10 per cent and different tungsten contents.

TABLE X

Composition of Steel.		Austenite.		Corresponding Eutectoid Carbon Content, Per Cent.	Hyper-eutectoid Amount of Carbon, Per Cent.
C Per Cent	W Per Cent.	C Per Cent.	W Per Cent.		
1.10	2	1.08	1.5	0.83	0 25
1.10	5	0.94	2 2	0.78	0 16
1.10	10	0.74	4.0	0.69	0 05

As is seen in a schematic way from the table, on increasing the tungsten content from 2 to 5 per cent in the steel the carbon content dissolved in the austenite decreases from 1.08 to 0.74 per cent. A consequence hereof, also shown by the table, is that *hyper-eutectoid steels approach the eutectoid composition when their tungsten content is raised.*

SUPPLEMENT, CONCERNING CARBIDES IN OTHER ALLOY STEELS

THE author has occasionally investigated some other alloy steels as to their carbide constituents. The following observations were made:

Chromium-tungsten. The *double carbide*, found in all high-speed steels of different chromium and tungsten contents, has the same etching characteristics as Z2 carbide of tungsten steels, and forms a similar rib-shaped eutectic. Probably it constitutes the same phase as Z2 and contains dissolved chromium.[1] It is, however, unlike Z2 of ternary tungsten steels, stable, probably because of the chromium content.

Chromium. In working for several years with chromium steels (C = 0.90 to 1.30 per cent, Cr = 1.0 to 2.0 per cent), the author never found any constituent, which on account of great hardness might be supposed to be chromium carbide. A *double carbide* is, however, found. not colored by boiling sodium picrate.

Molybdenum. In a Fe-Mo-C alloy, obtained as a laboratory melt, were found: one supposed *molybdenum carbide* and one or more supposed *double carbides*, one of which forms a rib-shaped eutectic with austenite similar to the austenite-Z2-eutectic. The molybdenum carbide is harder than cementite, but probably not as hard as WC. It appears in rounded grains.

Vanadium. The following steels, containing vanadium, were examined:

C = 1.35 per cent, V = 0.12 per cent;
C = 1.05 per cent, V = 0.25 per cent, Cr = 1.20 per cent;
C = 0.76 per cent, V = 1.55 per cent, Cr = 2.70 per cent, W = 17.7 per cent and other high-speed steels of a similar composition to this.

[1] It should, therefore, not be considered as a triple carbide.

All of them contained a supposed *vanadium carbide* in rounded grains, of a hardness comparable with that of molybdenum carbide. Therefore it may be concluded that vanadium has only a small solubility in austenite at high carbon content as well as in Fe-Cr-carbide and the Fe-W-Cr-carbide of high-speed steels. Consequently, it should not be expected that vanadium additions above a certain low limit add to the alloy steel qualities of a high-carbon steel.

In a Fe-V-C melt, especially made, vanadium carbide and probably some *double carbide* were found.

Titanium. In chrome steel, made with addition of ferro-titanium as well as in cast iron, containing titanium, angular grains of a hard constituent were noticed, very similar to WC, probably a *titanium carbide.*

Concluding from these observations, the metals above mentioned, considered as alloy metals for steel may be tentatively arranged as follows as to carbide forming properties: Chromium forms double carbide, but no single carbide; molybdenum forms double and single carbide; tungsten forms double and single carbide; vanadium forms single and possibly double carbide; titanium forms single (and possibly double) carbide.

It might be added that these conclusions, except concerning tungsten, are based merely upon microscopical evidences.

SUMMARY

THE results of the investigations made may be briefly summed up as follows:

(1) A number of tungsten steels and other iron-tungsten-carbon alloys of different compositions were examined in the microscope. From these investigations a tentative equilibrium diagram for the system Fe-W-C was constructed.

(2) The solubility of tungsten in the γ-iron phase, austenite, is limited at a certain tungsten content, above which a special constituent appears. This limit occurs at a lower tungsten content, as the carbon content increases.

(3) In Fe-W-C alloys of a carbon content corresponding to cast iron, the special constituent is cementite, containing dissolved tungsten to a varying extent, depending upon the total composition of the alloy. This cementite is stable over a certain range of composition.

(4) In tungsten steels with high carbon content, above about 0.7 per cent, the stable special constituent is WC, which has a hardness exceeding that of corundum and is not colored by boiling sodium picrate. At the junction between the cast iron and steel ranges the maximum tungsten content, dissolved in the austenite is probably below 1.5 per cent.

(5) In the same high-carbon tungsten-steel range, if the stable conditions are not reached, a metastable double carbide, called Z_2, appears. This carbide which is colored by boiling sodium picrate, forms a rib-shaped eutectic, of a characteristic appearance, with austenite.

(6) At carbon contents below about 0.7 per cent the special constituent is probably another double carbide, called Z_1, which is colored by boiling sodium picrate, but is distinguished from Z_2 by the shape of its eutectic with austenite. It is probably stable.

(7) At low carbon content the special constituent is prob-

ably an iron tungstide, which is colored by boiling sodium picrate.

(8) In studying the transformations in the solid state of tungsten steels of medium and high carbon content these were found, with the exceptions given below, to be of the same nature as those of carbon steels, i.e., the austenite decomposes on cooling into pearlite, which is preceded by ferrite separation in hypo-eutectoid, and cementite separation in hyper-eutectoid steels, the cementite and probably the ferrite also containing dissolved tungsten. The differences to be noticed when *ordinary* maximum temperatures are used, are the following:

(*a*) Tungsten raises the Ar_1 point (approximately 10° C. for each per cent W).

(*b*) Tungsten displaces the eutectoid composition of the austenite toward lower carbon content (approximately 0.05 per cents for each per cent W).

(*c*) Tungsten retards the pearlite transformation.

(*d*) The pearlite is finer than that of carbon steels.

(9) Furthermore, a special change in condition of the austenite of tungsten steels, here called *stabilization*, is brought about by heating to a *high temperature*, as found by many previous investigators. This stabilization of the austenite was studied by the author through numerous cooling experiments from different temperatures—910° to 1200° C.—the structures developed at different stages during cooling, being fixed by quenching. The results hereof are given in the following paragraphs, 10 to 16.

(10) The stabilization of the austenite appears essentially as a retardation of the pearlite transformation on cooling, so that this transformation occurs even on rather slow cooling at a lower temperature and at a slower rate, the retarding effect being promoted by raising the initial temperature, at least up to 1200° C., as well as by increasing the tungsten content and by decreasing the carbon content. At certain combinations of composition, initial temperature, and cooling rate, the pearlite transformation is completely suppressed.

(11) The position of the pearlite transformation point Ar_1

on exceedingly slow cooling is, however, not or possibly slightly lowered by previous heating to a high temperature.

(12) A result of the stabilization is that the austenite on cooling, except on very slow cooling, remains, partly or entirely untransformed, when a lower temperature—600° to 525° C.—is reached, at which ferrite is separated, at a considerable rate, even in steels with high carbon content, thereby increasing the carbon content of the austenite. This ferrite shows a Widmannstätten arrangement and has been called *secondary ferrite*. The secondary ferrite separation constitutes the lower critical point or " second pearlite point," found by previous investigators of tungsten steels.

(13) For a given composition, the temperature range of secondary ferrite separation has an upper limit, above which no ferrite is separated, even on extended soaking, but instead pearlite is slowly formed.

(14) If the stabilized austenite is kept for some time in the secondary ferrite separation range, an unknown constituent, called *streaks*, is formed. When etched in nitric acid solution, they appear as thin dark needles in Widmannstätten arrangement. These streaks may be slipbands, formed by deformation within the austenite grains, caused by the secondary ferrite separation.

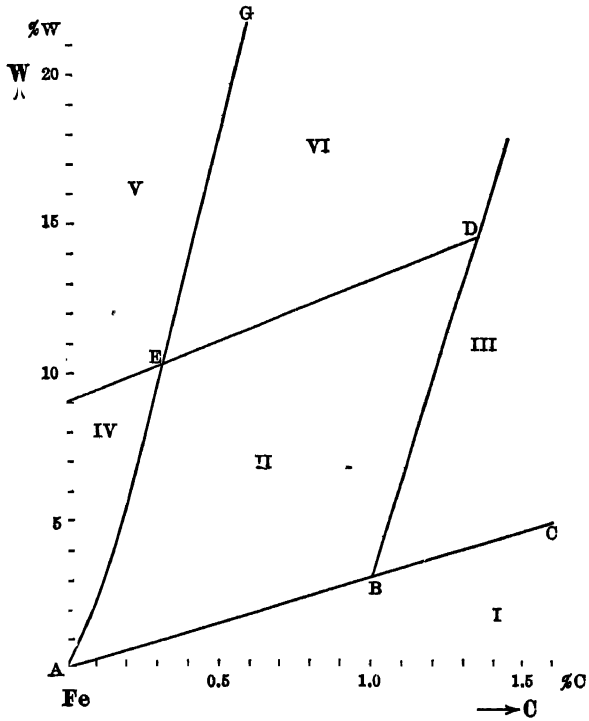
(15) After the secondary ferrite has separated, the stabilized austenite is, on further cooling, at about 500° C. or lower, subject to decomposition of an unknown nature, which is the more rapid and complete, the lower the tungsten content.

(16) Those parts of the austenite which remain untransformed pass into martensite on quenching, partly or entirely, even if the quenching temperature is as low as 500° C. This indicates that martensite is a constituent formed at a temperature lower than 500° C.

(17) Some practical consequences of the presence of free carbide in tungsten steels have been discussed.

(18) Some observations concerning carbides in other alloy steels have been given.

PLATE 3.



Equilibrium Diagram Fe–W-C according to Honda and Murakami

APPENDIX

INVESTIGATIONS ON TUNGSTEN STEELS BY HONDA AND MURAKAMI[1]

THESE investigators have made an extensive study of the equilibrium diagram, microstructure and transformations of tungsten steels. Their results and views will be reviewed in the following three chapters:

(1) Equilibrium diagram;
(2) Microstructure;
(3) Transformations.

(1) EQUILIBRIUM DIAGRAM

The equilibrium diagram of tungsten steels as given by Honda and Murakami[2] is shown in Plate 3 in such a form as to be comparable with the author's diagram. The same scale is used as in Plate 2.

In studying the diagram of Honda and Murakami, it should be borne in mind that it represents the equilibrium conditions, not at high temperature, when the iron is in the γ state (as does the author's tentative diagram) but at room temperature, that is to say, when iron is in the α state. Consequently the products of transformations occurring during cooling in the solid state are included in their diagram. The nature of these transformations and the composition of their products will vary with the maximum temperature applied before cooling and also with the rate of cooling, as will be shown later in relating Honda and Murakami's results of magnetic measurements. The diagram

[1] As mentioned on p. vi, it was not until finishing his own treatise the author learned of the existence of these investigations.

[2] "On the Structure of Tungsten Steels." The Science Reports of the Tohoku Imperial University, Vol. VI, No. 5, April, 1918, p. 235.

which is given by Honda and Murakami applies to the conditions brought about in normal cooling from about 850° C.

The phases or constituents of Honda and Murakami's diagram are the following:

Ferrite is assumed to be free from carbon and tungsten in low-tungsten steels. In high-tungsten low-carbon steels it is said to dissolve tungsten in the form of tungstide Fe_2W molecules up to 9 per cent tungsten.

Cementite is said to be pure Fe_3C. It has a magnetic transformation about 200° C.

Double carbide, as introduced by Honda and Murakami, is a carbide formed in cooling through Ar_1, not existing as free constituent above Ac_1. It has a magnetic transformation about 400° C. and is thereby distinguished from cementite. It forms with ferrite pearlite of a very fine structure and has no microscopical characteristics differing from those of cementite. Its probable composition as given by Honda and Murakami is $4Fe_3C \cdot WC$. This composition is not obtained by analysis of carbide residue. A residue, obtained from a magnet steel (W = 5.38 per cent, C = 0.63 per cent), slowly cooled from 900° C., was found to contain 8.10 per cent C., 31.71 per cent Fe and 53.70 per cent W.[1] This residue is said to be a partly decomposed mixture of WC and double carbide $4Fe_3C \cdot WC$, the presence of the latter being proved by magnetic heating and cooling curves taken on the residue itself. The question whether this carbide is a true double carbide or not, as well as its probable composition, will be discussed later in connection with the magnetic curves.

Tungsten carbide WC, according to Honda and Murakami, is not a free carbide present at high temperature (compare the author's results), but is formed in cooling in the solid state at Ar_1. It has no magnetic transformation. It was not observed in the microscope. In fact, not a single proof of its existence is given.

Tungstide of iron, Fe_2W, is the only free constituent besides austenite existing at high temperature according to Honda and

[1] "On the Thermomagnetic Properties of the Carbides Found in Steels," The Science Reports of the Tohoku Imperial University, Vol. VI, No. 1, June, 1917, p. 23.

Murakami. It was found in the microscopical examination of tungsten steels of high tungsten and low and medium carbon contents as well as of a number of alloys of the binary system iron-tungsten. It has no magnetic transformation. It is apparently identical with the author's Fe_nW. The composition given seems very probable from Honda and Murakami's results on iron-tungsten alloys.

As seen from Plate 3, Honda and Murakami divide the equilibrium diagram in six regions, denominated I-VI.

Only one dividing line is based upon microscopical evidence, viz., FED, separating regions V and VI from the other part of the diagram. In these two regions of high tungsten content, the free constituent Fe_2W was found to exist at high temperatures. Below this line, according to Honda and Murakami, all tungsten and carbon present are in solid solution in the austenite at high temperature. Neither any double carbide nor WC is said to exist free at high temperature. This does not well agree with the author's results as given in the tentative diagram, Plate 2. In low-carbon high-tungsten steels, corresponding to region V, the author found a constituent Fe_nW, apparently identical with Honda and Murakami's Fe_2W. At medium carbon content a somewhat different constituent was found, called Z1 by the author, believed to be a double carbide of low-carbon content. The possibility that this view is correct is still open. Furthermore, it is obvious, that Honda and Murakami have overlooked the existence of WC and double carbide Z2 proven by the author (see Plates 1 and 2) as free constituents at high as well as low temperature, the former representing the stable, the latter the metastable equilibrium in high-carbon tungsten steels. Hence Honda and Murakami pay no attention to the fact that in steels of a composition corresponding to their region III and probably parts of regions I and II, the solid solution through the presence of free carbide is displaced toward lower tungsten and also lower carbon contents.

Fe_2W being the only free constituent at high temperature, according to Honda and Murakami, the other characteristics of the diagram are results of the transformations in cooling the austenite to room temperature. These transformations and their

products are studied by Honda and Murakami mainly by their magnetic characteristics. The variation of intensity of magnetization with temperature in different steels is given in numerous curves, by the author referred to as magnetic cooling or heating curves. The transformations found and their significance are the following:

Magnetic transformation at 200° C. indicates presence of cementite Fe_3C.

Magnetic transformation at 400° C. indicates presence of double carbide $4Fe_3C \cdot WC$.

Magnetic transformation about 700° C. indicates presence of ferrite.

Thus the different regions are characterized by the following constituents:

I. Ferrite+double carbide+cementite.
II. Ferrite+double carbide+(tungsten carbide).
III. Ferrite+double carbide+cementite+(tungsten carbide).
IV. Ferrite+(tungsten carbide).
V. Ferrite+(tungsten carbide)+(tungstide).
VI. Ferrite+double carbide+(tungsten carbide)+(tungstide).

The constituents within parentheses are nonmagnetic, wherefore their presence is assumed for other reasons, viz.:

Tungstide is observed in the microscope.

Tungsten carbide, WC, not being seen in the microscope, nevertheless is assumed to be present whenever there is tungsten or carbon left over, which cannot be accounted for in any other way. For instance, region II contains more tungsten than can be absorbed by the double carbide, assuming its composition to be $4Fe_3C \cdot WC$ and the ferrite to be pure iron. Therefore part of the tungsten and carbon contents are assigned to form WC. The ferrite of regions I, II, and III is supposed to be pure iron, but that of regions IV, V, and VI to contain dissolved Fe_2W, in the latter two in a quantity corresponding to 9 per cent tungsten. There is no reason given why the ferrite of steel No. 22 (W = 6.83 per cent, C = 0.30 per cent), for instance, should contain no tungsten, that of steel No. 16 (W = 5.33 per cent, C = 0.12 per cent) assumed to contain all the tungsten dissolved, except

the amount, absorbed by the low carbon content. In fact it is a mathematical impossibility for steel No. 22 to consist of pure iron, WC, and $4Fe_3C \cdot WC$. In the author's opinion, it is very probable that all ferrite of the ternary system iron-carbon-tungsten contains dissolved tungsten to an extent varying with the tungsten and carbon contents.

The composition of the double carbide by Honda and Murakami is very uncertain, as will be seen from later discussion on p. 94. It should not be confused with the double carbides Z_1 and Z_2 of the author's diagram, the microscopical characteristics of which are given on p. 61.

(2) MICROSTRUCTURE

As mentioned above, the tungstide was observed by Honda and Murakami in the microscope. Its etching qualities are the same as those of Fe_nW described by the author. They did not, however, observe WC and double carbide Z_2.

As said before the double carbide of Honda and Murakami was not seen in the microscope as a separate constituent. It is said to form pearlite; this cannot, however, be distinguished from ordinary pearlite in tungsten steels.

Honda and Murakami contend that the eutectoid composition by the tungsten content is displaced towards higher carbon content. This being contrary to the view arrived at by the author, it would have been of interest to study Honda and Murakami's microphotographs in this respect. These are, however, taken mainly at low magnification and hence do not clearly illustrate this point. In this connection, the following two facts should be borne in mind as being of influence in judging the eutectoid composition of the austentite:

(1) The possible presence of secondary ferrite even at high carbon contents, and consequently not indicating hypo-eutectoid composition. The conditions for formation of secondary ferrite are described in the author's investigation.

(2) The presence of free carbide, in which case the carbon content of the austenite is lower than that of the steel as a whole.

The best way to settle the question of eutectoid composition

appears to be the studying of microstructures of different steels quenched immediately above Ac_1.

Globules observed by Honda and Murakami in high-carbon tungsten steels (e.g., W = 4.72 per cent, C = 1.57 per cent) are in their opinion cementite, not double carbide. From the author's investigation there is no doubt that a steel of this composition contains double carbide or WC (compare steels Wn6 and Wn7, p. 53). Hyper-eutectoid cementite is, of course, also present below its separation point. Honda and Murakami base their statement that double carbide is absent, also upon the fact that no magnetic transformation at 400° occurred on heating a quenched specimen of this steel. This fact is, however, not conclusive, since the double carbide of Honda and Murakami probably is different from the author's double carbide Z2.

Another point of interest, which is also studied by Honda and Murakami by microscopic examination, is the separation of ferrite about 550° C., by the author called secondary ferrite. Honda and Murakami also have observed the needle-shaped appearance of this ferrite as compared with the "granular" form of the ordinary ferrite. They explain the structure of the former as a result of heating to high temperature, whereby the granular ferrite dissolves tungstide, thus changing to acicular ferrite. This view is hard to understand, inasmuch as no ferrite exists above Ac_3. The author believes that the needle-shape as well as higher tungsten and carbon contents of the secondary ferrite are results of its low temperature of formation, the conditions of equilibrium, metastable as this probably is at this temperature, being necessarily different from those of the temperature, at which granular ferrite is formed (compare Fig. 3*a*).

From microstructures given by them, Honda and Murakami infer that the secondary ferrite separation is followed by a eutectoid transformation, the eutectoid being composed of ferrite containing tungstide and cementite. This eutectoid transformation is said to be a pearlite transformation displaced by the tungstide dissolved in the ferrite. They accordingly call this transformation Ar'_1. The microphotographs show large ferrite needles in a matrix containing smaller needles. Honda and Murakami's view would be correct if the areas between the

small needles were cementite. In similar structures studied by him, the author found that these areas in slowly cooled specimens became dark on etching in nitric acid solution and hence probably consisted of a decomposed solid solution. The fine needles of ferrite are therefore probably separation ferrite as well as are the larger needles, both being, separated before A'_1. It appears to be proved, however, from Honda and Murakami's magnetic curves, to be discussed later, that cementite is formed during the transformation A'_1, probably in a very fine state, not to be discerned in the microscope.

(3) TRANSFORMATIONS

In studying the transformations in tungsten steels, Honda and Murakami have made extensive use of measurements of intensity of magnetization in its variation with temperature. They present a great number of magnetic heating and cooling curves, which undoubtedly bring out new features of tungsten steels and greatly contribute to the knowledge of these steels.

In Plate 4 are reprinted a few representative examples of their magnetic cooling curves, taken on two steels, No. 5 (2.06 per cent W, 0.50 per cent C) and No. 25 (7.92 per cent W, 0.63 per cent C) cooled from different maximum temperatures and at different rates.

Let us first examine the curves obtained at a normal rate of cooling from different initial temperatures. From Fig. 30 curve 2 is seen how in cooling from 850° C. the $Ar_{3.2}$ transformation starts at 720° C., the Ar_1 transformation takes place at 660° C. and is there completed, whereupon in further cooling a magnetic transformation occurs at 400° C. When the initial temperature is raised to 900°, as seen from Fig. 31, curve 2, the transformation at 700° is incomplete, a second transformation sets in at 550° and is finished at 450° C., a third point occurs at 400° and a fourth at 200° C. According to the author's belief, the second point, by Honda and Murakami designated as Ar'_1 should more appropriately be called $Ar'_{3.2}+Ar'_1$ since the beginning of it probably signifies separation of secondary ferrite, the end being the decomposition of the remaining austenite.

In normal cooling from 1100° C., as seen from Fig. 32, curve 3, no transformation occurs until 580° C., this probably being $Ar'_{3\text{-}2}$, followed by Ar'_1, ending at 450° C. The 400° point is here absent, only the 200° point being visible on further cooling.

The magnetic cooling curves of steel No. 25, normal cooling from 900, 1000, 1100, and 1200° C. is shown in Figs. 33 to 36. The trend of these curves is similar to that of the curves just described.

As far as the transformations occurring above 400° C., are concerned, these curves show the same facts as were brought out by the author's cooling experiments, that is to say, when the initial temperature of cooling is raised the pearlite transformation is gradually diminished and finally suppressed. Suppressing of the pearlite transformation, partially or completely, is always accompanied by secondary ferrite separation $Ar'_{3\text{-}2}$, about 550° C. on further cooling, this being followed by decomposition of the remaining austenite. Both these transformations are by Honda and Murakami taken together and considered as one point Ar'.

When the further cooling is considered, the curves bring out new results. It is established by Honda and Murakami that the magnetic transformations at 400° and 200° signify magnetic critical points of carbides, the latter undoubtedly of cementite, the former of a carbide, found to be present in the residue of a magnet steel, cooled from 900° as described on p. 80. Since high tungsten content was found in this residue, it is claimed that this carbide is a double carbide. It might, however, as well be cementite of a higher tungsten content (see discussion on p. 89). At all events, the significant fact is that cementite alone is formed in cooling from high temperature and "double carbide" only from low-temperature (850°), whereas both appear on cooling from intermediate temperatures. Before relating Honda and Murakami's theory on these phenomena, their experiments with different rates of cooling as effecting the magnetic cooling curves will be dealt with. In each figure on Plate 4 one curve is given with the cooling carried out at a rapid rate. From these curves, considered together, is seen, that the Ar_1

transformation is practically suppressed in all of them, except in cooling steel No. 25 from 900° C. (Fig. 33, curve 3), when part of it is visible. Furthermore, the Ar'_1 transformation is by rapid cooling brought down to lower temperature, the higher the tungsten content and the higher the initial temperature. Finally, all these curves show the cementite transformation at 200° C., and not the "double carbide" transformation, except the curve just mentioned from cooling steel No. 25 from 900° C., in which both carbide points are seen.

In all curves, so far considered, at normal as well as at rapid cooling rate, a relation appears to exist between the Ar_1 and Ar'_1 transformations on one hand and the two carbide points on the other hand to that effect, that whenever Ar is present (i.e., a transformation above 600° C.), the carbide transformation at 400° C. appears and whenever Ar'_1, occurs (probably preceded by $Ar'_{3.2}$), it is always followed by the cementite transformation at 200° C. This is true whatever the initial temperature was. There is a seeming exception from this rule in curve 2 of Fig. 34, in which Ar_1 is seen above 600° and a second transformation about 550°, carbide transformation occurring about 380° only. This apparent discrepancy can, however, be explained by the supposition that the 500° transformation here is solely a secondary ferrite transformation, not followed by the Ar'_1 decomposition, but by martensite formation.

We will next consider Honda and Murakami's curves on slow cooling. Steel No. 5, when slowly cooled from 850° or 900° C. undergoes a complete Ar_1 transformation at 670° C., preceded by $Ar_{3.2}$ at 730° C., as seen from Figs. 30 and 31. In Fig. 32 are shown two curves with slow cooling from 1100° C., curve 1 with the cooling retarded between 720 and 670° C., showing Ar_1 at 675° and a carbide point at 370° and curve 2 with retarded cooling between 600 and 540° C., showing the $(Ar'_{3.2}+Ar'_1)$ point at 540° and the cementite point at 210° C. Comparing these two curves, it appears that the position of the carbide transformation, and therefore the nature of the carbide, as said above, depends upon whether the Ar_1, or the Ar'_1 point is brought to appear, the initial temperature in both curves being the same.

Steel No. 25 gives the following results on *slow* cooling, as seen from Figs. 33 to 36:

Cooling from 900° C. gives Ar_1 at 650° and a carbide point at 400° C.

Cooling from 1000° C. gives Ar_1 at 700° and a carbide point at 260° C.

Cooling from 1100° C. gives Ar_1 at 700° and a carbide point at 270° C.

Cooling from 1200° C. gives Ar_1 at 700° when retarded from 750 to 700° C. and about 450° when retarded from 600 to 450° C., in both cases a carbide transformation occurring at 200° C. on further cooling. These results are somewhat peculiar in regard to the values of the carbide transformation temperature obtained (260–270° C., as compared with 200 and 400°) and are different from the results with steel No. 5 in that respect that the Ar_1 transformation at 700°, brought about by slow cooling from 1000° C. or higher temperature, is not succeeded by a carbide transformation at 400° C. but at 260, 270, and 200°, respectively, all of which by Honda and Murakami are assumed to signify the transformation of cementite.

At this point the question arises, whether, as Honda and Murakami contend, the carbide transformations can be regarded as indicating the presence of either or both of two definite carbides, one being cementite, Fe_3C, the other double carbide, $4Fe_3C \cdot WC$. In this respect, it is of interest to note actual values of carbide transformation obtained in Honda and Murakami's numerous cooling curves. Among the points given as cementite transformations, values from 150 to 270° C., are found, and for "double carbide" values from 360 to 450° C. Although some of the low values may be due to rapid cooling, it still seems plausible, in the author's opinion, to assume, that the two carbides actually are one, viz., cementite with different contents of dissolved tungsten, the tungsten content varying with the temperature of formation.[1] A support for this theory is to be

[1] In this connection it is interesting to study the results of magnetic investigations of chrome steels by Murakami, published in the paper: "On the structure of iron-carbon-chromium alloys," the Science Reports of the Tohoku Imperial University, Vol. VII, No. 3, Dec., 1918, p. 217. From his magnetic

found in the fact that the cementite formed in melts, containing iron, tungsten and carbon, appeared to contain dissolved tungsten (or possibly tungsten carbide) in considerable amount (compare p. 62). A parallel may here be drawn with the carbon content of the austenite in a carbon steel. As is well known, the austenite at very high temperature, i.e., in equilibrium with melt, contains only a low carbon content. This content gradually increases up to about 1.8 per cent when the temperature is lowered, until the eutectic temperature about 1130° C. is reached. On further cooling the austenite is in equilibrium with cementite and accordingly its carbon content gradually decreases to about 0.9 per cent at the eutectoid temperature 700° C. If similar conditions hold good for the cementite of tungsten steels, the following factors affecting its tungsten content have to be borne in mind:

(1) The composition of the austenite:
(2) With which phase (austenite or ferrite) the cementite is in equilibrium;
(3) Whether the equilibrium is stable or metastable;
(4) The temperature, at which cementite is formed.

cooling curves on chrome steels the following carbide transformations may be quoted:

Composition of Steel.		Carbide Transformation.
Cr Per Cent.	C Per Cent.	° C.
...	0.28	200
0.44	0.28	150
0.86	0.98	150
2.83	1.05	None

Murakami ascribes the 200° transformation to cementite, the 150° transformation to a double carbide α and contends that the absence of magnetic carbide transformation in the last steel is due to the presence of a nonmagnetic double carbide.

In the author's opinion cementite is present in all the steels quoted, that of the chrome steels containing chromium dissolved. Hereby the gradual lowering of the magnetic carbide transformation with increasing chromium content is explained. Thus, at sufficiently high chromium content the cementite transformation is brought down below room temperature.

If the cooling curves on Plate 4 are considered in the light of this theory, we find the following:

If the Ar_1 transformation occurs about 700° C., the austenite is decomposed into ferrite with low tungsten and carbon contents and cementite of high tungsten content, the latter on further coo ing undergoing its magnetic transformation in the vicinity of 400° C. If the austenite reaches 550° C. untransformed the $Ar'_{3.2}$ transformation takes place, ferrite with high tungsten and carbon content being separated, after which the remaining austenite about 500° C. decomposes ($A'r_1$) into ferrite of high tungsten and carbon contents and cementite of low tungsten content, the latter on further cooling having its magnetic transformation in the vicinity of 200° C. Thus curve 2 of Fig. 34 is explained by ascribing the carbide transformation, about 400° C. to the cementite formed at 700° to 600 C., whereas the transformation at 550° C. is $Ar'_{3.2}$ and consequently does not produce any cementite. In curve 1 the specimen was cooled with slow rate from 770 to 700° C. This curve shows a carbide transformation at 260° C. This may be explained the following way. The Ar_1 transformation at 700° produced cementite of high tungsten content, but the cementite being metastable and a long time at this temperature being allowed, it decomposed into WC+cementite of low tungsten content. The same reasoning can be applied to curve 1 of Fig. 35 and curve 1 of Fig. 36. In order to verify this theory experiments such as the following would be valuable. Cooling curves should be taken from the same initial temperature, say 1000° C. In the first curve the temperature shou d be held at 700° for a sufficient time to allow the Ar_1 transformation to be completed, not more. The carbide transformation will then probably occur about 400° C. If in other experiments the time at 700° is increased to two, three, four hours, etc., it will on further cooling be seen whether the cementite firstly formed will decompose and give a cementite of lower tungsten content, as can be seen from the position of the carbide transformation on further cooling.

For explanation of the transformations visible in their numerous magnetic curves, a small part of which the author has quoted above, Honda and Murakami have built up a complicated

theoretical system, which now will be related. The basic principle of their theory is, that reactions going on and equilibrium attained between molecules dissolved in the austenite are responsible for the kind of transformation which occurs during cooling and consequently for the kind of carbide which is then set free. The equilibrium within the austenite varies with the temperature. They assume, that after heating just above Ac, all tungsten present (except the free tungstide of regions V and VI, see Plate 3) is dissolved in austenite as WC molecules. The carbon amount, which is not consumed by WC, forms Fe_3C molecules also dissolved. In cooling from this temperature at a normal rate, the Ar_1 transformation takes place and proceeds as follows: The two carbides combine and form double carbide $4Fe_3C \cdot WC$, the magnetic transformation of which is at 400° C., as seen on further cooling. Since the double carbide requires a definite proportion of tungsten to carbon, there is usually part of either component in excess. This is accounted for by formation of WC or Fe_3C at the same time as the double carbide forms. Whether the combination of WC and Fe_3C takes place while they still are in solution in the austenite or immediately after they have been set free, is not clearly stated.

If the temperature is raised to about 900° C., a reaction is said gradually to proceed within the austenite according to the formula: $WC + 5Fe = Fe_2W + Fe_3C$. This, it is claimed, is due to the fact that carbon has greater affinity for tungsten than for iron at low temperature, the opposite being true at higher temperature. Accordingly the reaction proceeds further at higher temperatures than 900° C. and is completed at 1100° C. in tungsten steels of low and medium carbon content, but requires still higher temperature for completion, when the carbon content is high. For this temperature the term "lowering temperature," introduced by Swinden may be used. Consequently, according to Honda and Murakami at the lowering temperature all tungsten exists as Fe_2W dissolved in the austenite and all carbon as Fe_3C also dissolved in the austenite. No WC exists, either dissolved or free. If the steel be cooled from the lowering temperature at a normal rate, no transformation occurs at 700° C., but due to the tungstide Fe_2W dissolved in the austenite, the

Ar_1 transformation is lowered to about 500° C. At this temperature ferrite, with dissolved tungstide, and cementite are formed, the latter undergoing its magnetic transformation at 200° C. on further cooling.

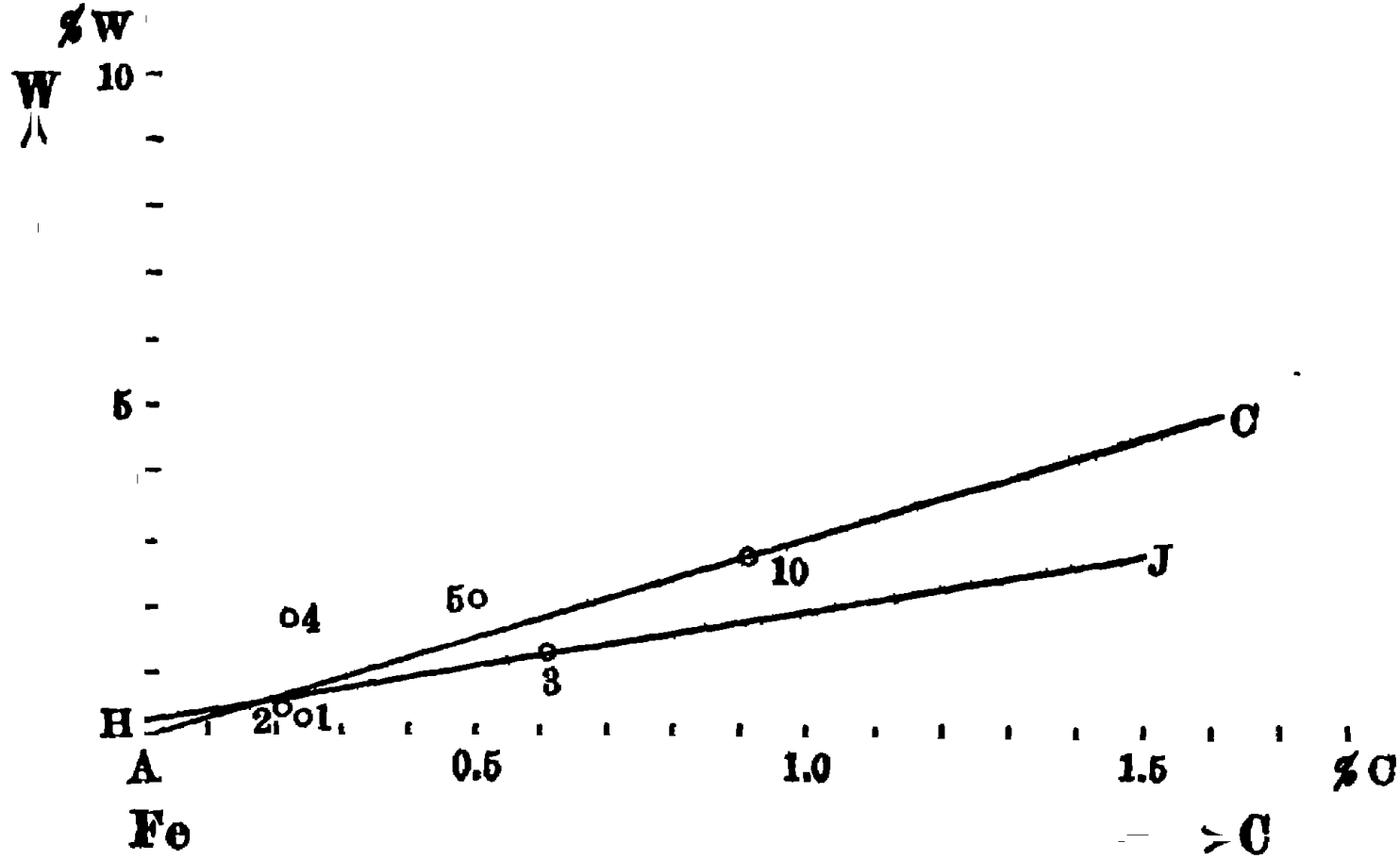
At temperatures between 900° C. and the lowering temperature both WC, Fe_3C, and Fe_2W molecules are dissolved in the austenite, according to this theory. Therefore on cooling a double transformation takes place. WC and Fe_3C form double carbide at Ar_1, but the portions of austenite, which contain Fe_2W dissolved, do not have their transformation until at Ar'_1, when cementite is set free.

The fact that steels rapidly cooled from 850° do not show the 400°, but the 200° transformation, is by Honda and Murakami explained so, that the WC and Fe_3C molecule do not have time to combine to double carbide.

If a specimen be cooled from the lowering temperature at an extremely slow rate through 700° C. the Ar_1 transformation takes place at this temperature. This, according to Honda and Murakami is due to the fact, that a reaction opposite to the one given above takes place within the austenite—the tungstide, formed at the high temperature, gradually changes to tungsten carbide and free iron, and at the same time, the A_1 transformation gradually proceeds. One would here expect that double carbide would be formed according to their theory, but such is not the case, as seen from the cooling curves 1 of Figs. 34 to 36. At least, one would expect, that if cementite is formed on slow cooling as in Fig. 34, curve 1, double carbide should not be formed on normal cooling from the same initial temperature as in Fig. 34, curve 2, since double carbide is supposed to be formed by combination of WC and Fe_3C. No explanation is given of this discrepancy between facts and theory.

If the "stabilizing" effect of heating to high temperature were due to the chemical reaction: $WC+5Fe=Fe_2W+Fe_3C$ within the austenite, it would reasonably be expected that the reaction be brought to proceed in the opposite direction by a prolonged soaking at 800° C. This should then have as its effect a comparatively rapid pearlite transformation about 700° C. No such effect was, however, noticed in soaking steel

PLATE 5.



B3, previously heated to 1200° C., for 10½ hours at 800° C., as stated on p. 17. It showed the same slowness in transformation as when continuously cooled from 1200° C.

Honda and Murakami also present heating and cooling curves on specimens quenched above Ac_1 and consequently martensitic. The heating causes tempering of the martensite and accordingly the heating curve shows a gradual increase of magnetization with increasing temperature.

If, when the temperature 500° C. is reached, a cooling curve is taken, the latter will show the nature of the carbide produced in tempering. This was always found to have its transformation at 200° C., wherefore Honda and Murakami draw the conclusion that cementite and not double carbide is present at the temperature of quenching, e.g., 900° C. They do not consider the fact that the austenite during quenching undergoes the transformation to martensite. According to the author's view it would be inferred that cementite, formed from martensite in tempering hardened tungsten steels, has a low tungsten content.

As said before, Honda and Murakami attribute the magnetic transformation at 400° C. to a double carbide of the probable composition $4Fe_3C \cdot WC$. They arrive at this composition by studying the magnetic cooling curves from low initial temperature of different tungsten steels and by applying the following reasoning: Steel No. 2 (0.44 per cent W, 0.21 per cent C., see Plate 5) shows on cooling from 807° C., two magnetic carbide transformations, one at 400° C., and one (weak) at 200° C. They conclude that it contains both cementite and double carbide. The same holds good for steel No. 3 (1.39 per cent W, 0.61 per cent C), when cooled from 859° C. Steels Nos. 4 (1.9 per cent W, 0.22 per cent C.), 5 (2.00 per cent W, 0.50 per cent C) and 10 (2.84 per cent W, 0.91 per cent C) show on cooling from 825, 862, and 862° respectively, only the 400° transformation, and are accordingly said to contain no cementite, only double carbide. Since they apparently assume that the ferrite of all these steels contains no tungsten—which hardly agrees, however, with their statement that ferrite can dissolve up to 9 per cent tungsten—it is logical to find the probable composition of the double carbide by drawing a line AC in the diagram from

pure iron in such a direction that steels containing cementite and double carbide fall below this line and steels containing no cementite fall above or on this line. In the former case WC should be present beside the double carbide. In this way and assuming the double carbide to have the formula $nFe_3C \cdot WC$, they find n to have the probable value 4. This is, however, a rather arbitrary calculation, as seen from the following. Steel No. 1 (0.23 per cent W, 0.23 per cent C) shows no double carbide transformation in the cooling curve from 810°. Following Honda and Murakami's theory, it should be inferred that the tungsten content is present as dissolved in the ferrite. In the other steels some tungsten may be present in the ferrite also, probably to varying amount. Thus any line to be drawn toward the prospective double carbide should emanate not from A, but from a point on the AW axis. As to the direction of the line the following may be observed. Steel No. 3 shows on cooling from 859° C. a conspicuous 400° transformation and a minute 200° transformation. In agreement with the general tendency of these curves it might be assumed, that on cooling from 800° C. no 200° transformation would appear. The line consequently should go through or below point 3 in the diagram. As the line AC now is drawn it passes steel No. 10 (see Plate 5) in the diagram. If the cooling curves of this steel are studied it is seen, however, that a maximum cooling temperature of 1102° must be reached before the 200° transformation appears in the curve, all curves from temperatures below this showing the 400° transformation only. Strictly following Honda and Murakami's theory this would appear to involve that the tungsten content, 2.84 per cent, could be lowered considerably, the carbon content 0.91 per cent remaining before the 200° transformation would be visible in the cooling curve from 800° C. A line like HT (see Plate 5) would therefore be more in accordance with the facts brought out by Honda and Murakami's cooling curves. This line would give the probable composition of the supposed double carbide to be about $7Fe_3C \cdot WC$. However, there does not seem to be sufficient reasons to believe that this carbide has a definite composition to be expressed by a chemical formula. Possibly it is cementite with dissolved WC. Moreover, it does

not appear permissible to draw a line to find the composition of this carbide, as long as the composition of the ferrite is not known.

In concluding it may be stated, that Honda and Murakami's investigations have brought out new and interesting features of the transformations in tungsten steels. The theories given by them, however, appear to be unnecessarily complicated and do not agree with some of their own, as well as the author's results. The suggestions, offered by the author, in order to explain the magnetic transformations found under different cooling conditions should be considered as tentative.

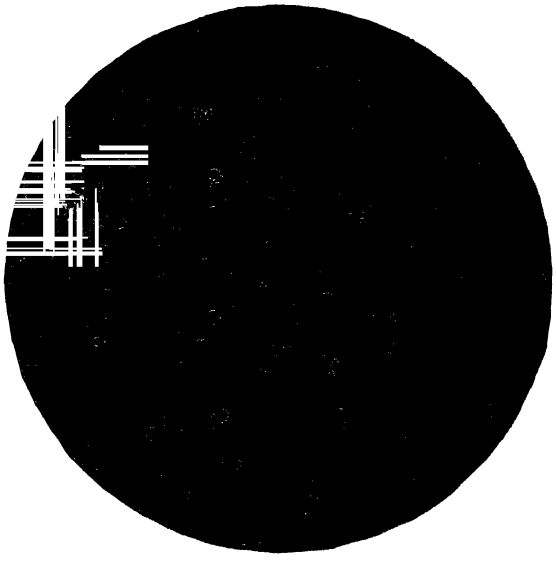


PHOTO NO. 1. ×500.

B3. 910° furnace 900° Q. HNO_3.

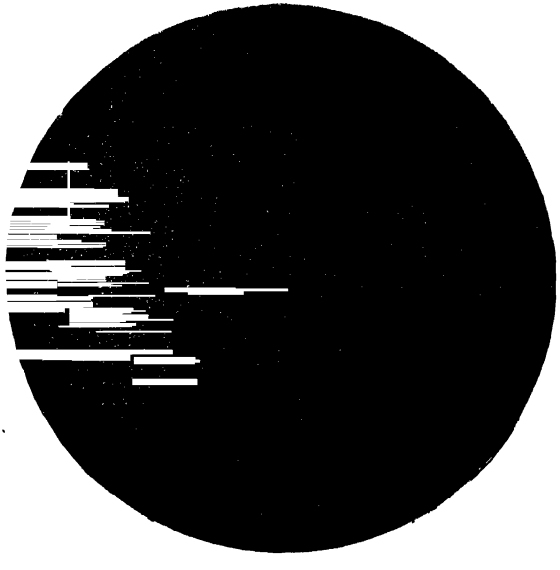


PHOTO NO. 2. ×500.

B3. 910° furnace 644° Q. HNO_3.

PHOTO NO. 3. ×1200.

BS. 910° furnace 725° 2h. Q. Sodium picrate.

PHOTO NO. 4. ×500.

BS. 910° furnace 715° 2h. Q. HNO_3.

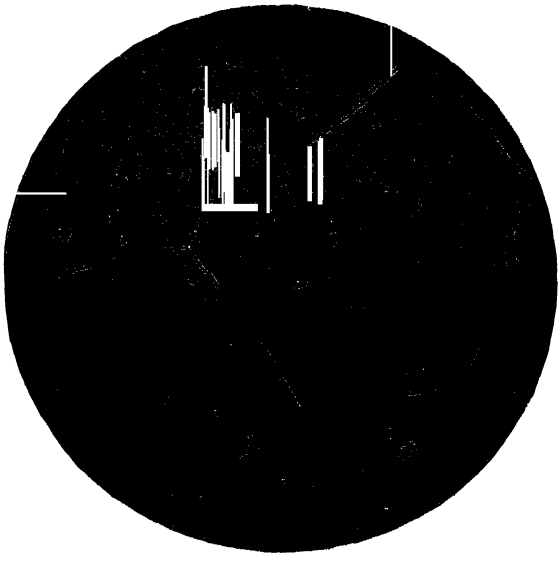


PHOTO NO. 5. ×500.

B3. 1200° furnace 720° Q. HNO_2.

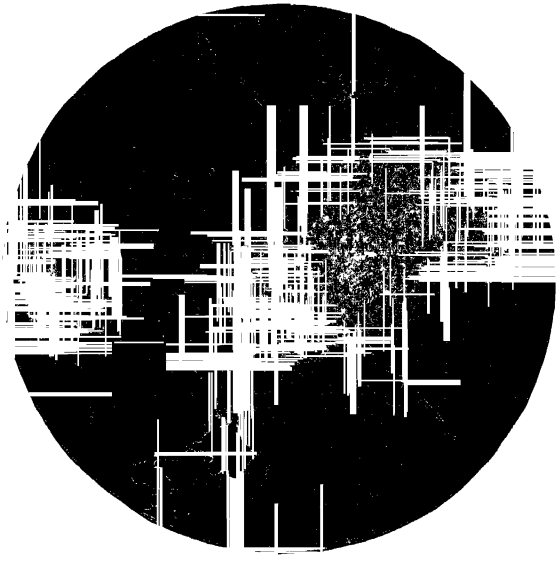


PHOTO NO. 6. ×500.

B3. 1200° furnace 650° Q. Sodium picrate.

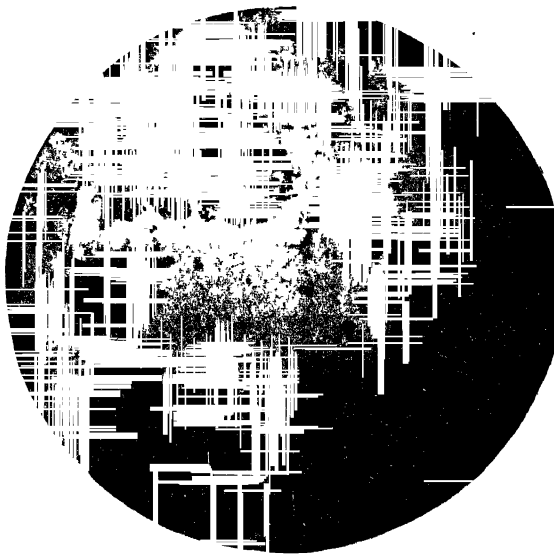


PHOTO NO. 7. ×500.

B3. 1200° furnace 584° Q. HNO_3.

PHOTO NO. 8. ×150.

B3. 1200° furnace 540° Q. HNO_3.

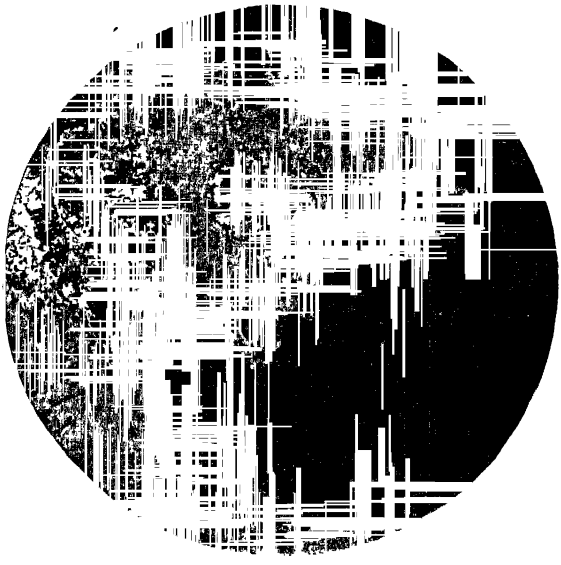


PHOTO NO. 9. ×500.

83. 1200° furnace 540° Q. HNO_3.

PHOTO NO. 10. ×1200.

83. 1200° furnace 540° Q. HNO_3.

PHOTO NO. 11. ×500.

B3. 1200° furnace 540° Q. Decarbonized surface portion. HNO_3.

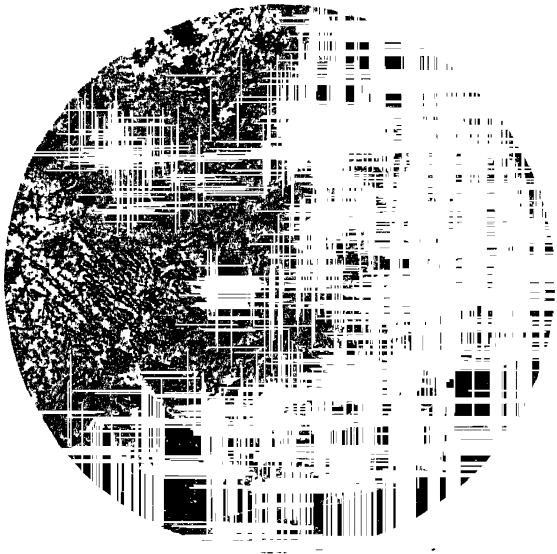


PHOTO NO. 12. ×500.

B3. 1200° furnace 515° Q. HNO_3.

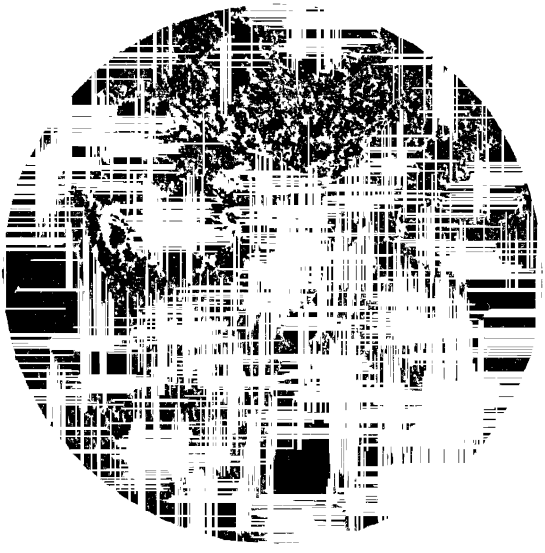


PHOTO NO. 13. ×500.

BS. 1200° furnace 500° Q. HNO_3.

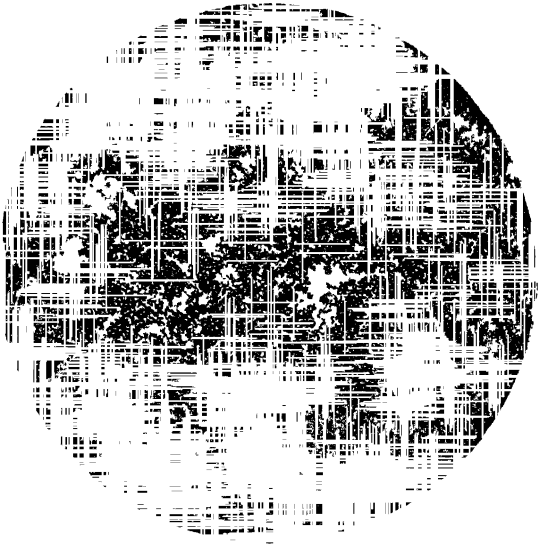


PHOTO NO. 14. ×500.

BS. 1200° furnace 600° 1h. Q. HNO_3.

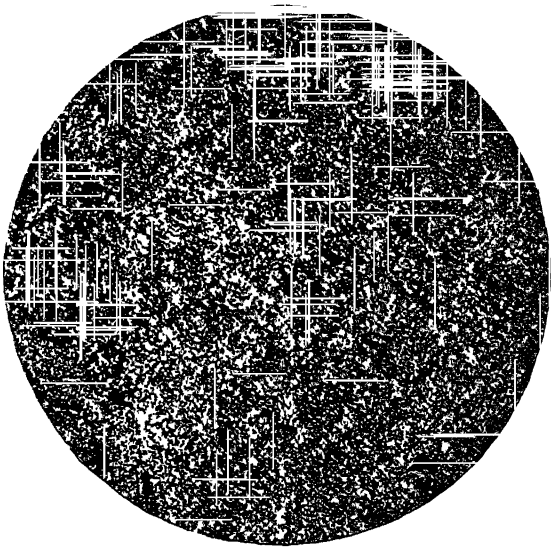


PHOTO NO. 15. ×500.

B3. 1200° furnace 600° 3h. Q. HNO_3.

PHOTO NO. 16. ×500.

B3. 1200° furnace 710° 1h. Q. Sodium picrate.

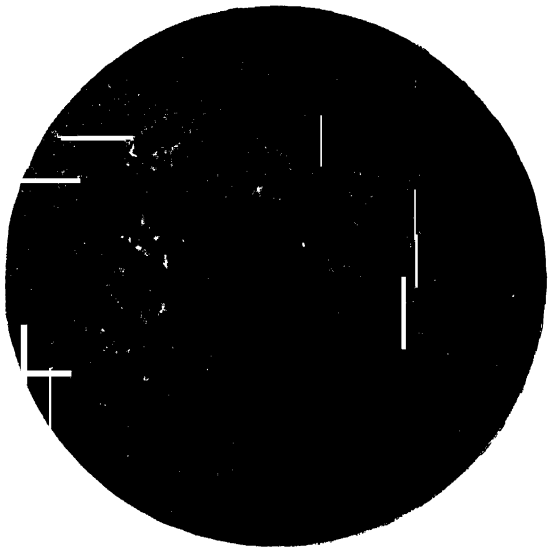


PHOTO NO. 17. ×1000.

B3. 1200° air 575° 15 min. Q. Sodium picrate

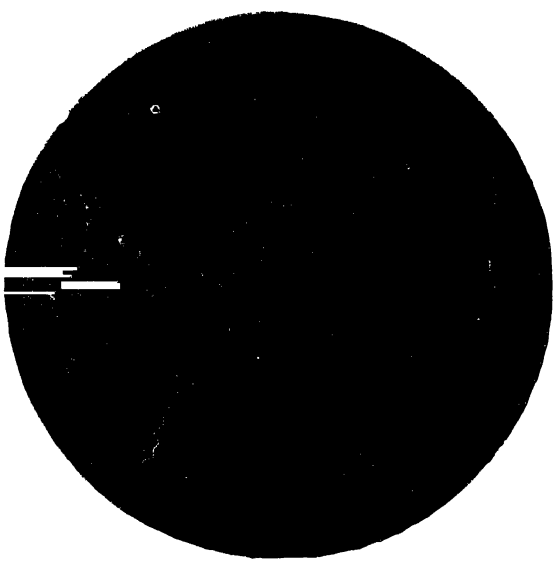


PHOTO NO. 18. ×1000.

B3. 1200° air 550° 15 min. Q. Sodium picrate.

PHOTO NO. 19. ×500.

B5. 1200° Q. HNO_3.

PHOTO NO. 20. ×1200.

B5, 1200° Q. HNO_3.

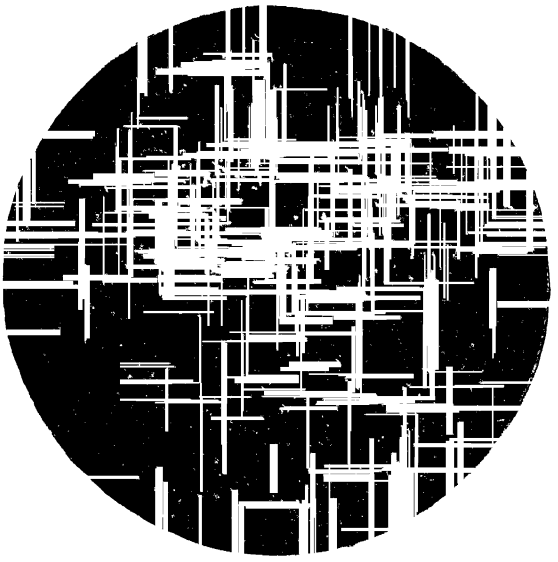


PHOTO NO. 21. ×500.

B5. 1200° furnace 550° Q. Center. HNO_3.

PHOTO NO. 22. ×500.

B5. 1200° furnace 550° Q. 1.5 mm. beneath the surface. HNO_3.

PHOTO NO 23. ×500.

B5. 1200° furnace 550° Q. 0.5 mm. beneath the surface. HNO_3.

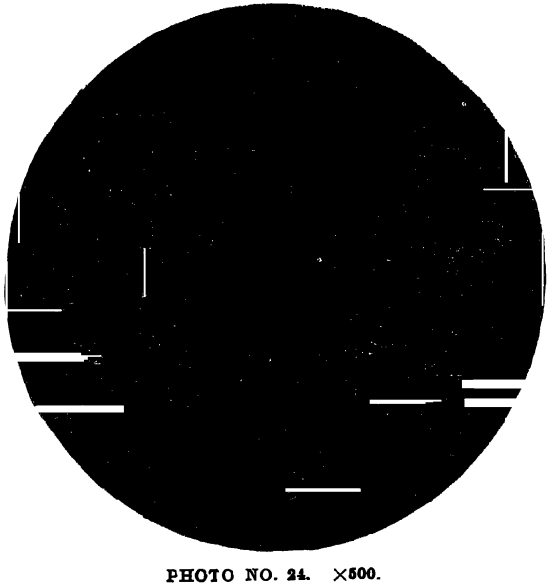


PHOTO NO. 24. ×500.

B5. 1200° air 550° 15 min. Q. HNO_3+sodium picrate.

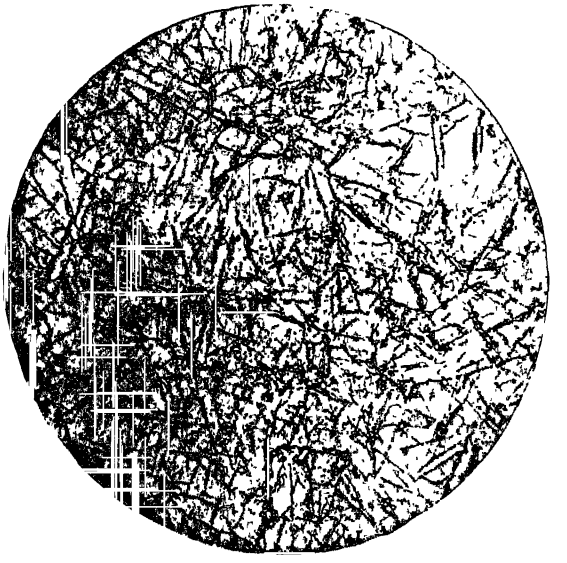


PHOTO NO. 25. ×500.

B5. 1200° air 525° 15 min. Q. HNO_3+sodium picrate.

PHOTO NO. 26. ×1200.

B5. 1200° air 525° 15 min. Q. HNO_3+sodium picrate.

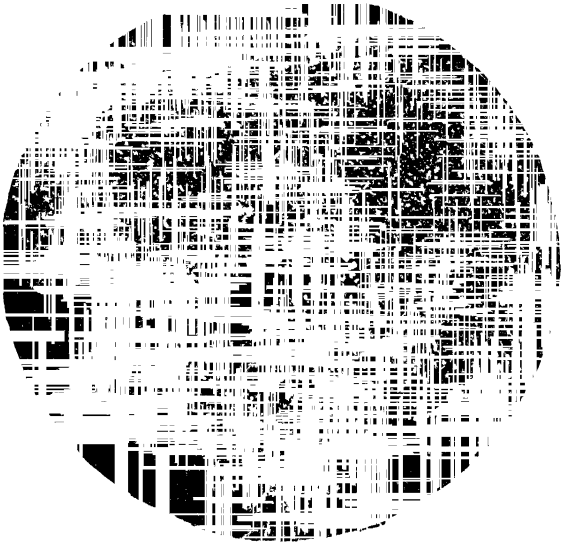


PHOTO NO. 27. ×500.

B5. 1200° air 500° 15 min. Q. HNO_2+sodium picrate.

PHOTO NO. 28. ×1200.

B2. 1200° furnace 705° 3h. Q. HNO_2.

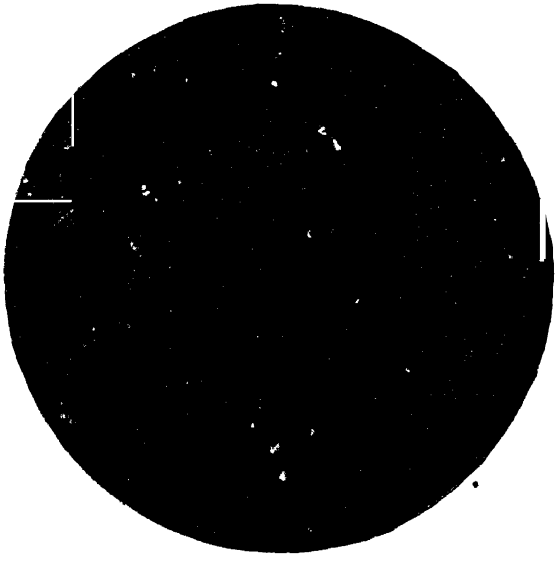


PHOTO NO. 29. ×600.

6. 1200° Heat tinted.

PHOTO NO. 30. ×500.

6. 1200° furnace 600° Q. HNO_3.

PHOTO NO. 31. ×500.

6. 1200° furnace 500° Q. HNO_3.

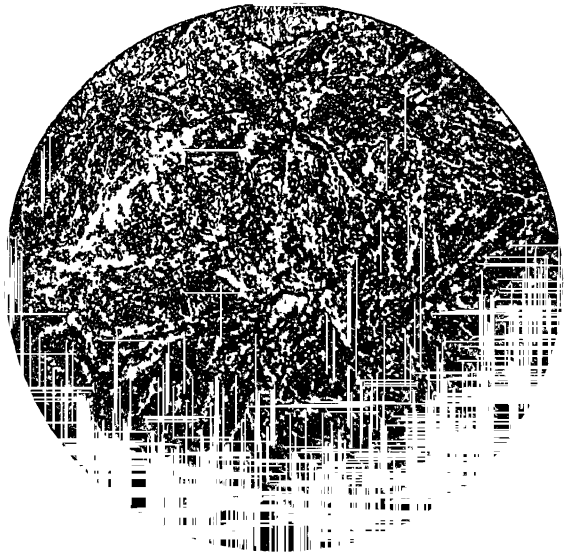


PHOTO NO. 32. ×500.

6. 1200° furnace 450° Q. HNO_3.

PHOTO NO. 33. ×500.

6. 1200° furnace 750° 2h. Q. HNO_3.

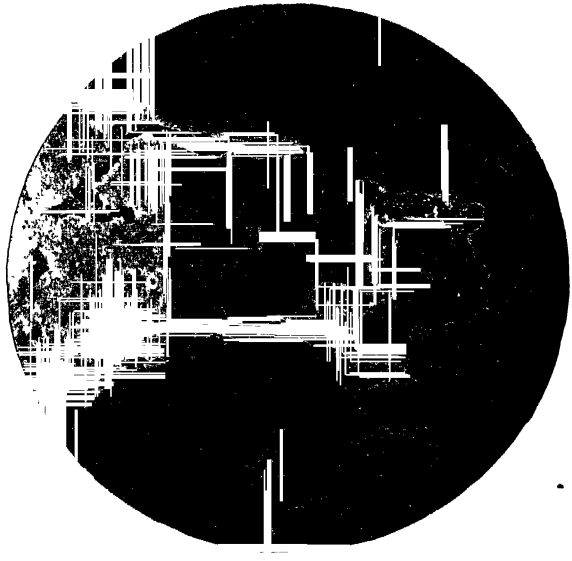


PHOTO NO. 34. ×500.

6. 1200° furnace 730° 2h. Q. HNO_3.

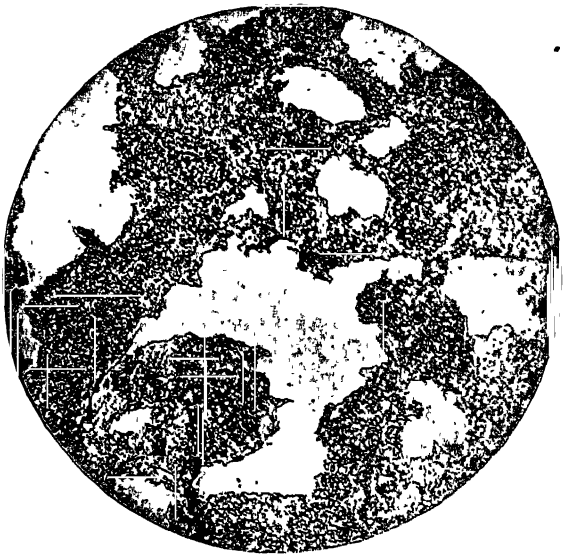


PHOTO NO. 35. ×500.

6. 1200° furnace 730° 2h. furnace 715° 2h. Q. HNO_3.

PHOTO NO. 36. ×500.

6. 1200° air 600° ½ h. Q. HNO_3.

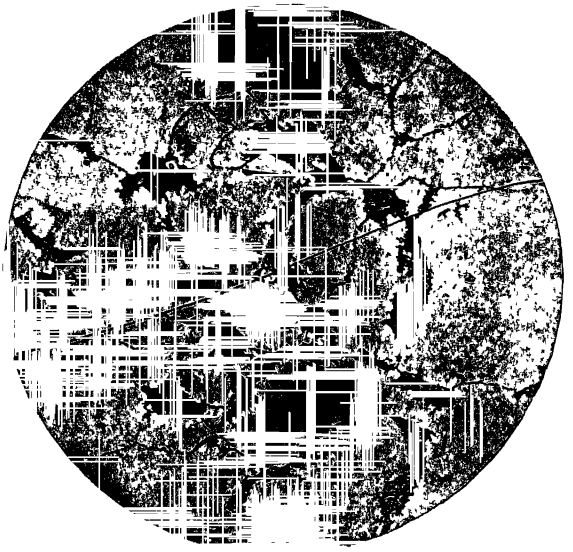


PHOTO NO. 37. ×500.

6. 1200° air 600° 5h. Q. HNO_3.

PHOTO NO. 38. ×500.

6. 1200° air 525° 15 min. Q. HNO_3.

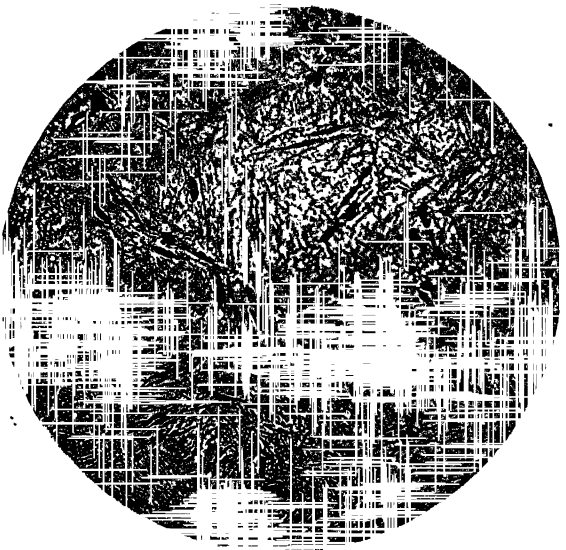


PHOTO NO. 39. ×700.

6. 1200° air normal temperature. HNO_3.

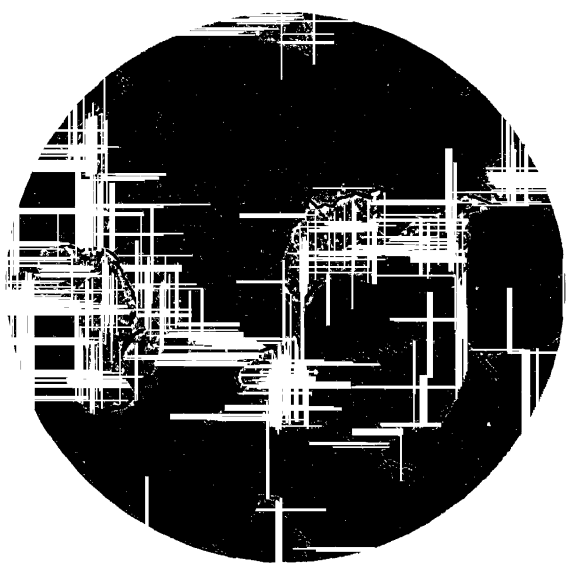


PHOTO NO. 40. ×500.

A. 1200° furnace 750° ½ h. Q. HNO_3.

PHOTO NO. 41. ×500.

A. 1200° air 625° 10 min. Q. HNO_3.

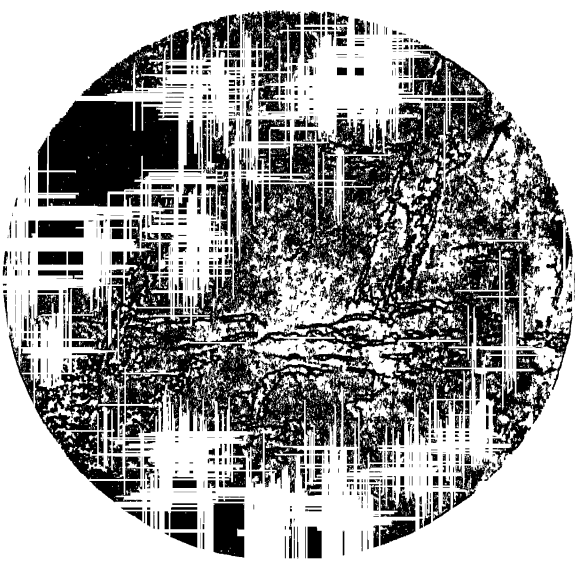


PHOTO NO. 42. ×500.

A. 1200° air 575° 10 min. Q. HNO_3.

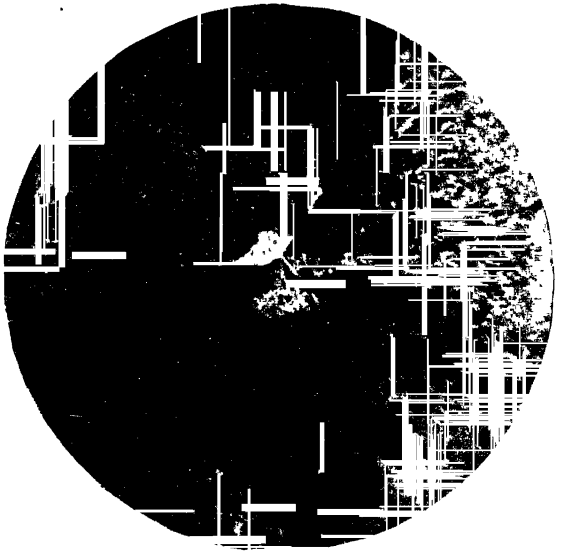


PHOTO NO. 43. ×1200.

6. Carburized. Center. HNO_3.

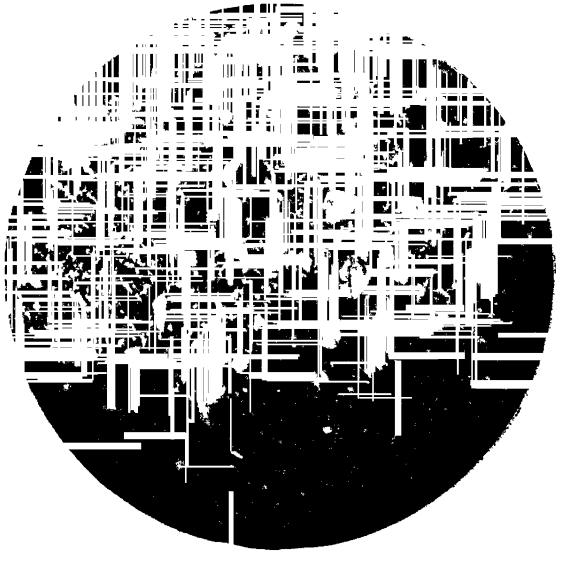


PHOTO NO. 44. ×1200.

6. Carburized. Center. HNO_3.

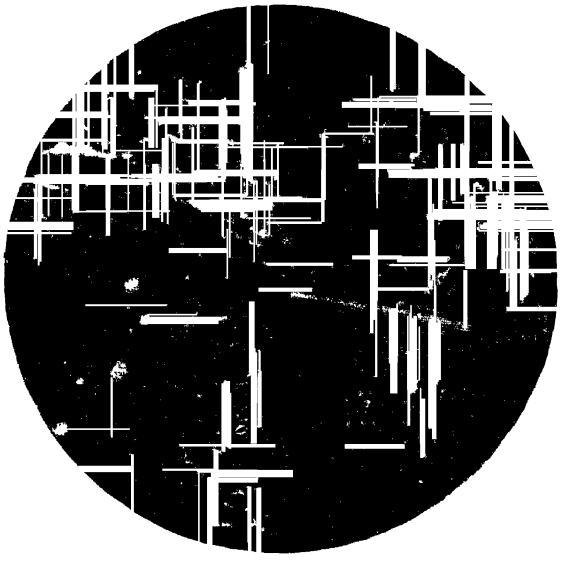


PHOTO NO. 45. ×1200.

6. Carburized. Just below surface. HNO_3.

PHOTO NO. 46. ×1200.

6. Carburized. In immediate surface. HNO_3.

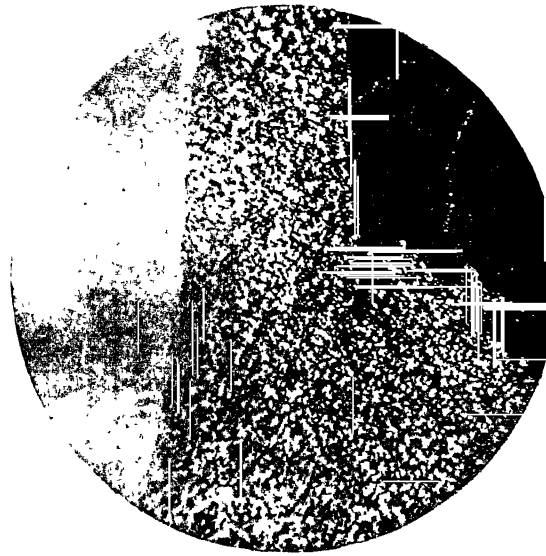


PHOTO NO. 47. ×150.

Welded specimen tungsten with soft iron 0.04 per cent C. Heat tinted.

PHOTO NO. 48. ×1200.

Welded specimen tungsten with soft iron 0.04 per cent C. Heat tinted.

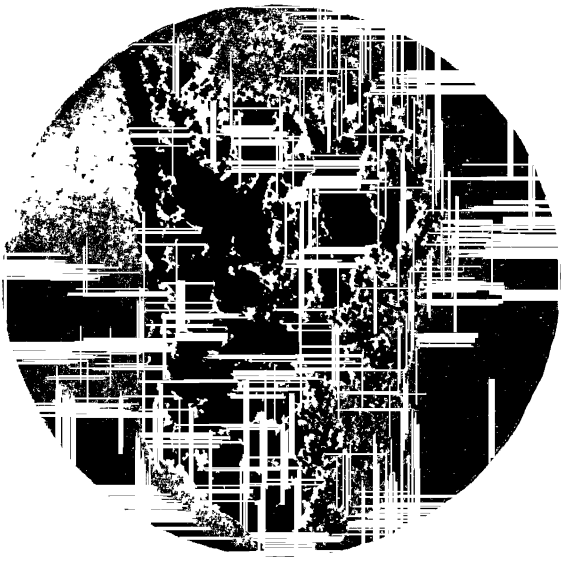


PHOTO NO. 49. ×500.

Welded specimen tungsten with soft iron 0.04 per cent C. Sodium picrate.

PHOTO NO. 50. ×500.

Welded specimen tungsten with steel 0.90 per cent C. Heat tinted.

PHOTO NO. 51. ×1200.

Welded specimen tungsten with steel 0.90 per cent C. Heat tinted.

PHOTO NO. 52. ×1200.

Welded specimen tungsten with steel 1.79 per cent C. Heat tinted.

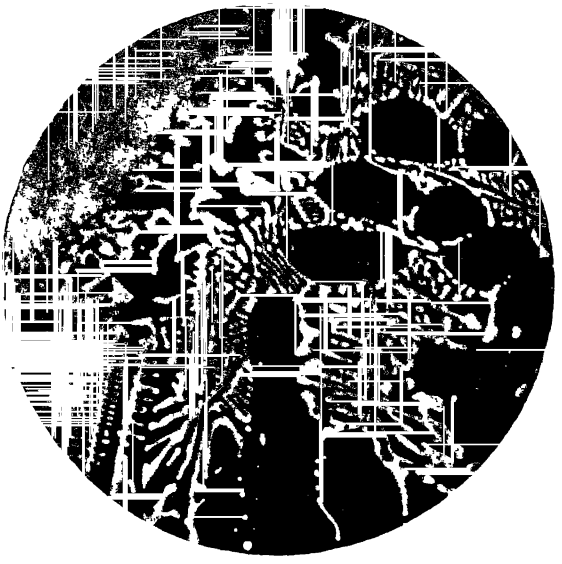


PHOTO NO. 53. ×1200.

Welded specimen tungsten with steel 1.79 per cent C. Heat tinted.

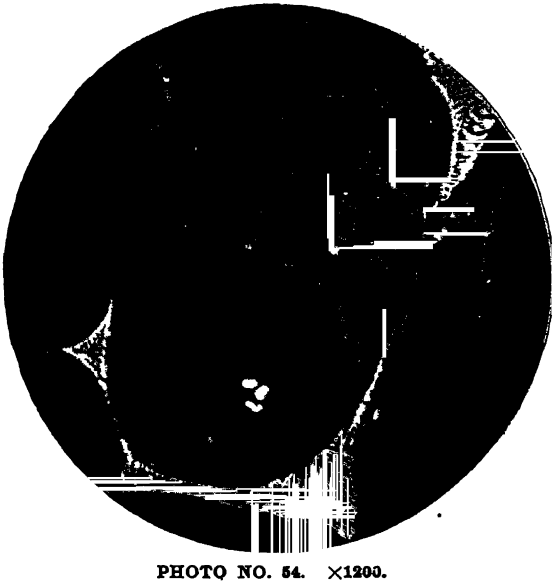


PHOTO NO. 54. ×1200.

Welded specimen tungsten with steel 1.79 per cent C. Heat tinted.

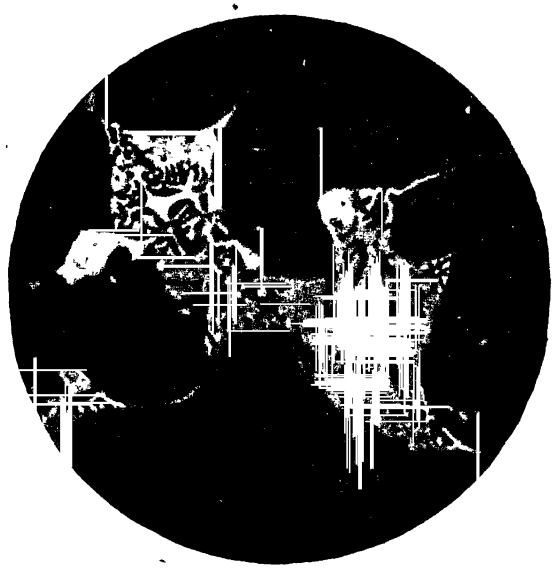


PHOTO NO. 55. ×1200.

Welded specimen tungsten with steel 1.79 per cent C. Heat tinted.

PHOTO NO. 56. ×1200.

Welded specimen tungsten with steel 1.79 per cent C. Heat tinted.

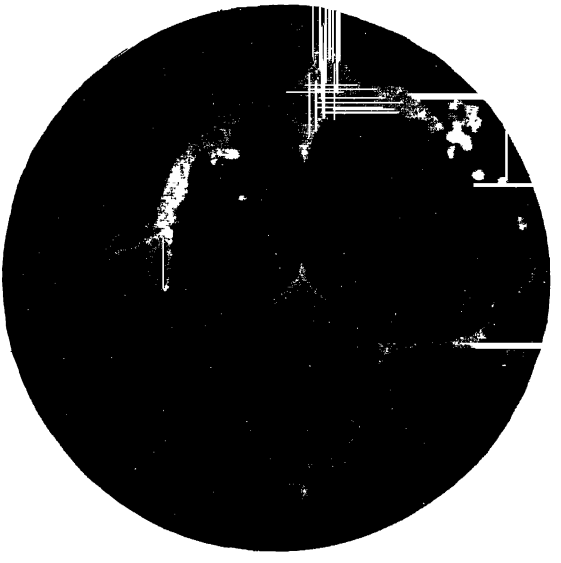


PHOTO NO. 57. ×1200.

Welded specimen tungsten with steel 1.79 per cent C. Heat tinted.

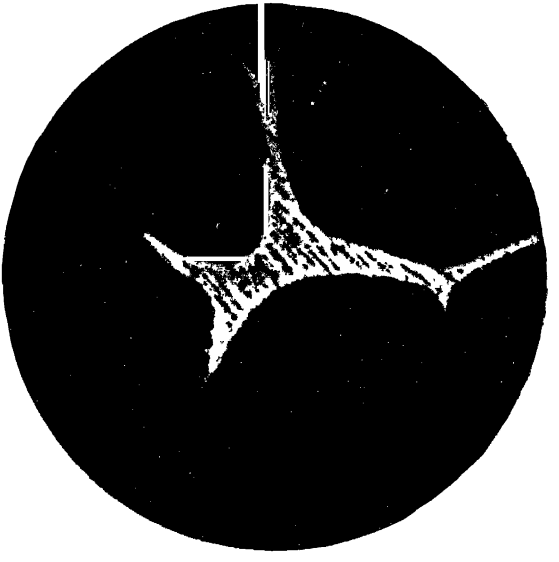


PHOTO NO. 58. ×1200.

Welded specimen tungsten with steel 1.79 per cent C. Heat tinted

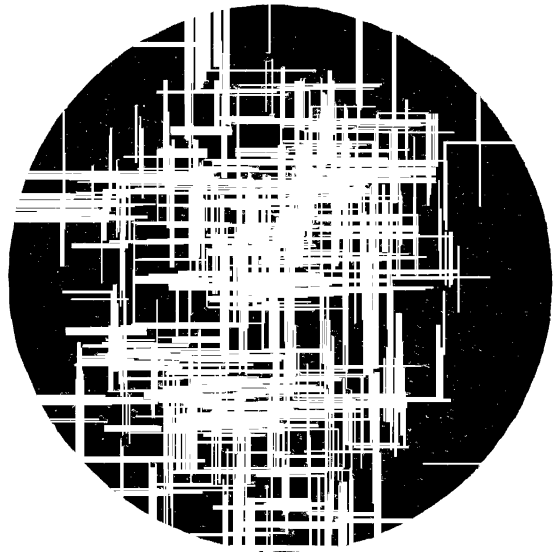


PHOTO NO. 59. ×150.

Welded specimen tungsten with cast iron 3.1 per cent C. Heat tinted.

PHOTO NO. 60. ×1200.

Welded specimen tungsten with cast iron 3.1 per cent C. Heat tinted.

PHOTO NO. 61. ×1200.

Welded specimen tungsten with cast iron 3.1 per cent C. Heat tinted.

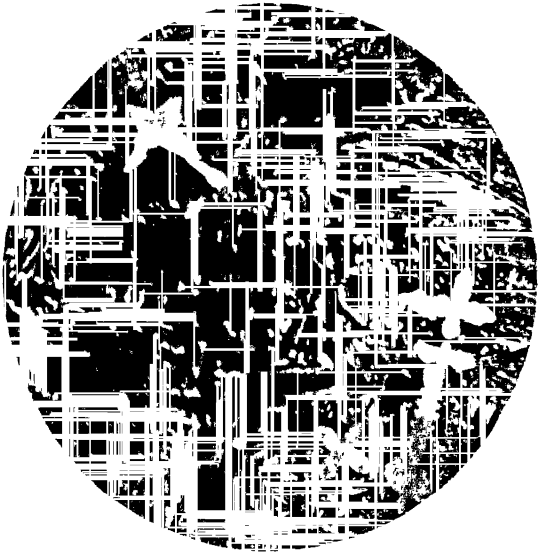


PHOTO NO. 62. ×1200.

Welded specimen tungsten with cast iron 3.1 per cent C. Heat tinted.

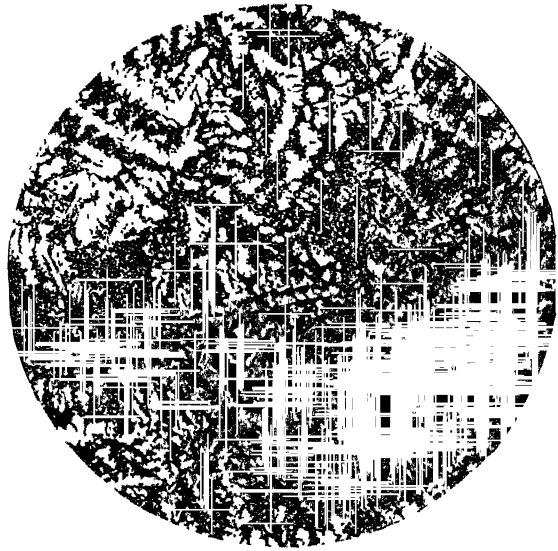


PHOTO NO. 63. ×500.

Welded specimen tungsten with cast iron 3.1 per cent C. Heat tinted.

PHOTO NO. 64. ×500.

Welded specimen tungsten with cast iron 3.1 per cent C. Heat tinted.

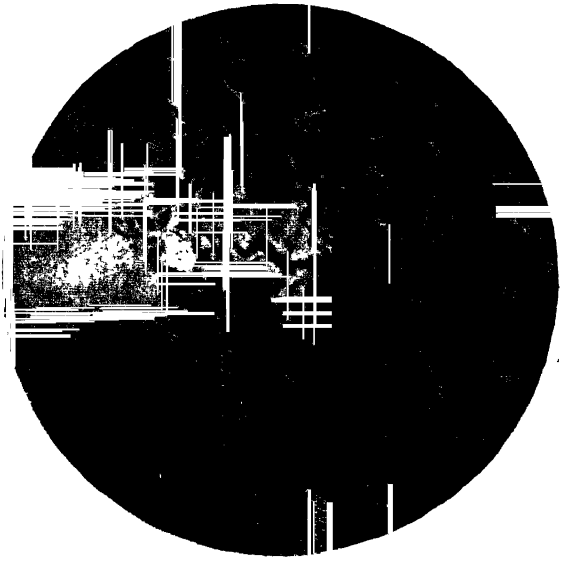


PHOTO NO. 65. ×1200.

Welded specimen tungsten with cast iron 4.1 per cent C.

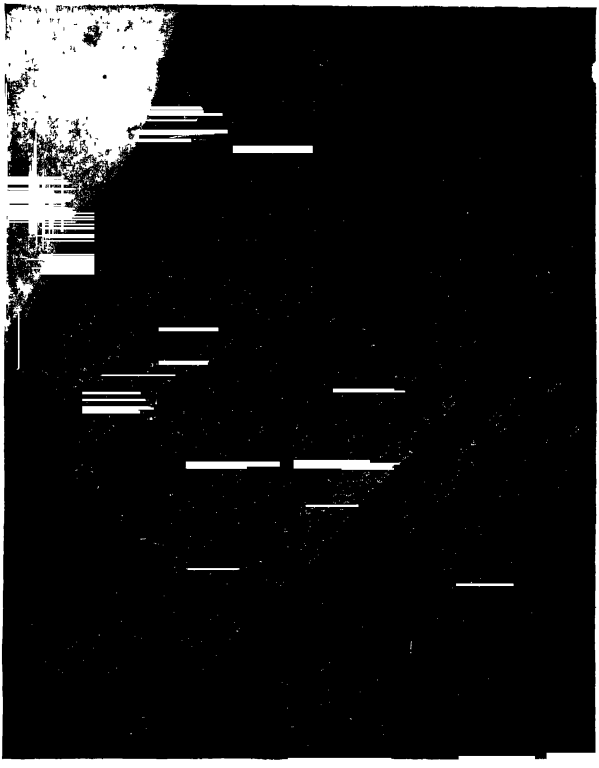


PHOTO NO. 66. ×150.

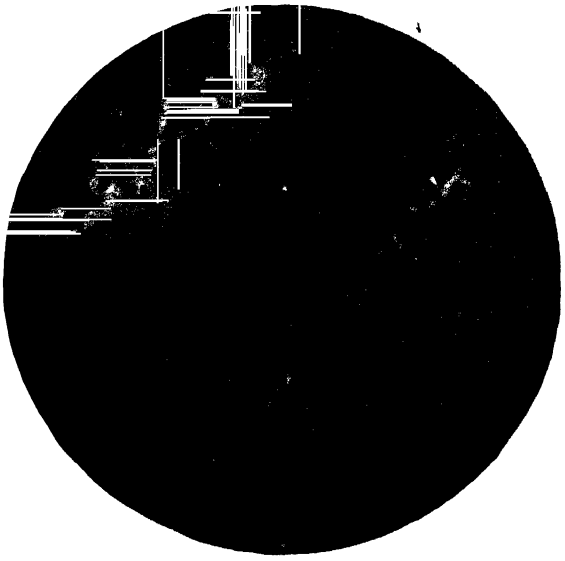


PHOTO NO. 67. ×1200.

Welded specimen tungsten with cast iron 4.6 per cent C. Heat tinted.

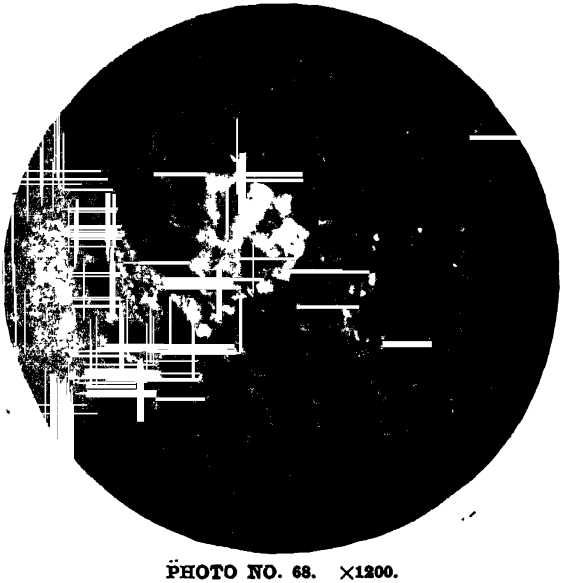


PHOTO NO. 68. ×1200.

Welded specimen tungsten with cast iron 4.6 per cent C. Heat tinted.

PHOTO NO. 69. ×1200.

Welded specimen tungsten with carbon. Heat tinted.

PHOTO NO. 70. ×100.

D. Soaked for 23hrs. at 1050° C. Q. Center. HNO_3.

PHOTO NO. 71. ×1200.

D. Soaked for 23hrs. at 1050° Q. Center. HNO_3.

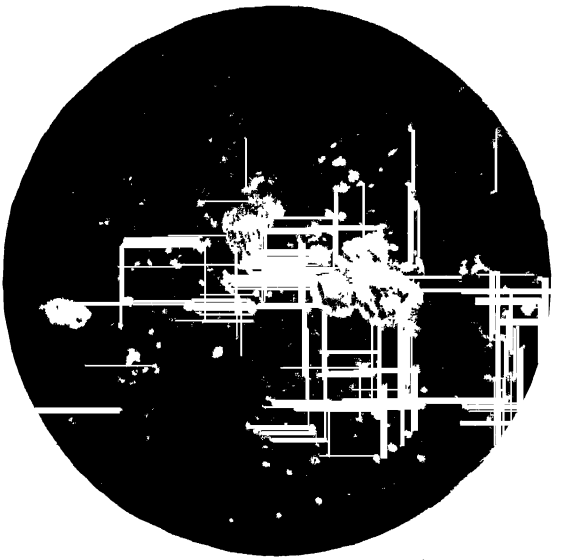


PHOTO NO. 72. ×1200.

D. Soaked for 23hrs. at 1050° C. Q. Slightly below surface. Heat tinted.

PHOTO NO. 73. ×150.

H. Heat tinted.

PHOTO NO. 74. ×150.

H. Heat tinted.

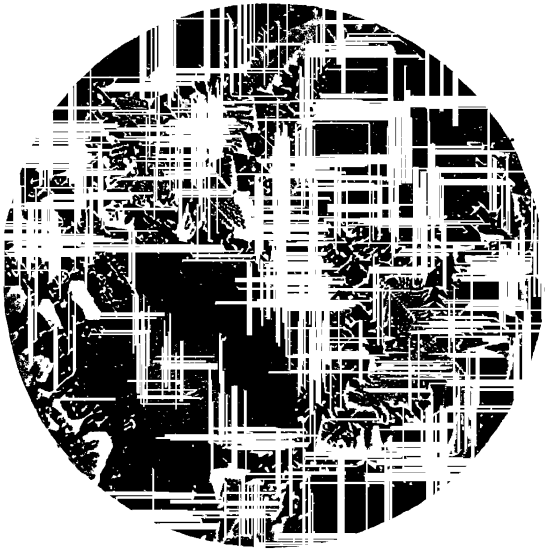


PHOTO NO. 77. ×150.

H. Heat tinted.

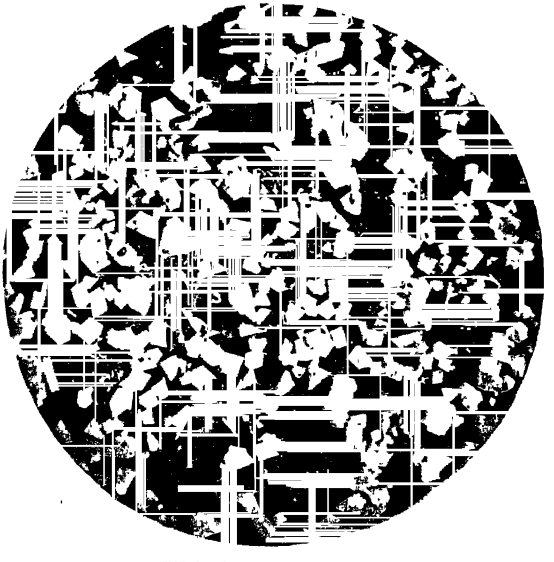


PHOTO NO. 76. ×150.

H. Heat tinted.

Wiley Special Subject Catalogues

For convenience a list of the Wiley Special Subject Catalogues, envelope size, has been printed. These are arranged in groups—each catalogue having a key symbol. (See special Subject List Below). To obtain any of these catalogues, send a postal using the key symbols of the Catalogues desired.

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(Over)

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